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## THE ALLOTROPY AND SOLUBILITIES IN WATER OF AMMONIUM BROMIDE.

BY ALEXANDER SMITH AND HERBERT E. EASTLACK.

Received May 8, 1916.

### Introductory.

Wallace,<sup>1</sup> using cooling-curve, dilatometric, and optical methods, observed that ammonium chloride and ammonium bromide undergo enantiotropic transformation at  $159^{\circ}$  and  $109^{\circ}$ , respectively. The chloride has recently been more carefully studied by Scheffer.<sup>2</sup> He finds from heating and cooling curves that the transformation takes place between the limits  $187^{\circ}$  (heating) and  $174^{\circ}$  (cooling). Determination of the solubility of ammonium chloride in water from  $160^{\circ}$  to  $205^{\circ}$  gave two curves intersecting at  $184.6^{\circ}$ , the transition temperature.

Before Scheffer's paper appeared, we had obtained similar results with the chloride from heating and cooling curves. The same method applied to the bromide had shown the transformation to take place at  $143\text{--}144^{\circ}$  on heating, while for the cooling curves the temperature varied from  $119^{\circ}$  down to about  $107^{\circ}$ . An experiment in which the thermometer and salt were sealed in a glass tube with a small amount of water (only the vapor phase, however, being in contact with the bromide) showed a

<sup>1</sup> *Centralblatt Min. Geol. u. Paläontol.*, 1910, 33.

<sup>2</sup> *Proc. Akad. Wetenschappen*, 18, 446 (1915); *C. A.*, 10, 411 (1916).

change on cooling at about  $130^{\circ}$ . The transition temperature for the bromide thus lay between the limits  $130^{\circ}$  and  $143^{\circ}$ . The low temperature reported by Wallace may be due either to an error in the calibration of his thermocouple, or more probably to supercooling, since the transformation in both cases is very sluggish.

The more exact determination of these two transition temperatures was in progress when Scheffer's paper came to our notice. In as much as his work had fixed with sufficient accuracy the transition point of the chloride, we completed only the determination of the transition temperature of the bromide, by measuring the solubilities of the salt in water over a temperature range sufficient to include the transition point.

In making the solubility determinations from  $100$  to  $170^{\circ}$ , it was observed that our curve was not a continuation of the one given by the solubility tables, all of which take their data from an article by Eder.<sup>1</sup> Consequently the determinations were carried on down to  $0^{\circ}$  in order to give a complete solubility curve for ammonium bromide.

### The Experimental Method.

The sealed tube method, which has been widely used in the investigation

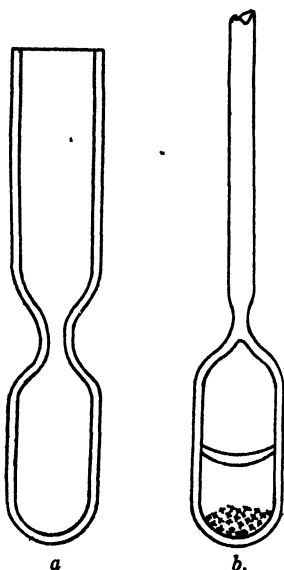


Fig. 1.—(Linear dimensions = actual size.)

of freezing point or solubility curves of various systems<sup>2</sup> where one of the components has a high vapor pressure, was the only method practicable for the present investigation.

A piece of soft glass tubing about 1 cm. in diameter was constricted and closed at one end (Fig. 1a) forming a bulb of about 1 cc. capacity. The volume of the bulb, required in calculating the weight of water in the vapor phase, was determined by weighing the tube empty and filled to the constriction with water. After the tube was carefully dried a small amount of ammonium bromide, which has been recrystallized from distilled water, sublimed *in vacuo* and dried at  $110^{\circ}$ , was introduced into the bulb and the tube was again weighed. An approximate weight of distilled water was then added, the bulb sealed off at the constriction and finally the two parts were weighed. A short length of glass rod was then fused on to the bulb (Fig. 1b) and

served to support the bulb in the bath.

<sup>1</sup> Ber. K. Akad. Wiss., Wien, [2] 82, 1284 (1880).

<sup>2</sup> Cf. Etard, Ann. chim. phys., [7] 2, 511 (1894), Kurloff, Z. physik. Chem., 23, 547 (1897), Hartley, J. Chem. Soc., 89, 1015 (1906), Tyer, THIS JOURNAL, 97, 622 (1910), Kendall, Ibid., 36, 1227 (1914), Smits and Bokhorst, Z. physik. Chem., 89, 374 (1915).

# CONTENTS TO VOLUME XXXVIII.

L. J. Curtman and P. Daschavsky: A Study of the Silver Arsenate Test for Arsenic.....	1330
William Blum: The Determination of Aluminium as Oxide.....	1332
Graham Edgar: The Estimation of Vanadic Acid after Reduction by Metallic Silver.....	1297
Aswini Kumar Datta and Nirlatan Dhar: Constitution of Chromic Acid. Part I.....	1303
Note: A Bottle for the Iodimetric Titration of Copper.....	1308

## Organic and Biological.

James Kendall: The Addition Compounds of Phenols with Organic Acids.....	1309
Harry Shipley Fry: VI. Further Evidence for the Electronic Formula of Benzene and the Substitution Rule.....	1323
Harry Shipley Fry: VII. The Action of Sodium Methylate upon the Products of Nitration of Ortho-, Para- and Meta-Chlorotoluenes.....	1327
Harry Shipley Fry: VIII. Further Evidence for the Electronic Tautomerism of Benzene Derivatives.....	1333
William J. Karlslake and Perry A. Bond: 4-Nitro-5-methyl-2-sulfobenzoic Acid and Some of its Derivatives.....	1338
Marston Taylor Bogert and John Ross Tuttle: The Synthesis of <i>p</i> -Cymene 2-Monocarboxylic Acid and of <i>p</i> -Cymene 3-Monocarboxylic Acid, together with Certain of their Derivatives.....	1349
Harry Essex, Harold Hibbert and Benjamin T. Brooks: The Hydrolysis of Chloropentanes as Affected by High Pressure: Synthetic Fusel Oil.....	1368
G. MacArthur and I. V. Burton: Brain Cephalin. II. Fatty Acids.....	1375
W. E. Bach and Wilmer C. Gangloff: The Action of Anhydrous Aluminium Chloride upon Unsaturated Compounds.....	1382
Treat B. Johnson and A. Willard Joyce: Researches on Pyrimidines. LXXVIII. The Reduction of 2-Mercapto-6-chloropyrimidines.....	138
Treat B. Johnson and Arthur J. Hill: Studies of Nitrated Proteins: V. The Hydrolysis of Nitro-Fibroin with Hydrochloric Acid.....	139
G. A. Russell: Volatile Oil of <i>Euthamia Caroliniana</i> (L) Greene.....	139
B. B. Turner: The Chemical Composition of <i>Oscillaria Prolifica</i> .....	140
James B. McNair: The Poisonous Principle of Poison Oak.....	141
S. F. Acree: On the Constituents of Poison Ivy ( <i>Rhus toxicodendron</i> ).....	142
H. S. Grindley and H. C. Eckstein: The Nonprotein Nitrogenous Constituents of Feedingstuffs.....	142
C. S. Hudson and J. K. Dale: The Isomeric Pentacetates of Glucosamine and of Chondrosamine.....	143
New Books: Chemistry in the High School; "Changes in the Food Supply and their Relation to Nutrition".....	143

## August.

### General, Physical and Inorganic.

I. H. Derby and Victor Yngve: The Dissociation Tensions of Certain Hydrated Chlorides and the Vapor Pressures of Their Saturated Solutions.....	143
Joel H. Hildebrand: Solubility.....	143
Farrington Daniels: An Adiabatic Calorimeter.....	147
James Kendall: The Specific Conductivity of Pure Water in Equilibrium with Atmospheric Carbon Dioxide.....	144
C. James and P. S. Willand: The Rare Earth Cobalticyanide.....	144

## CONTENTS TO VOLUME XXXVIII.

Alexander Smith and Herbert E. Eastlack: Ammonium Iodide, Its Solubilities and the Absence of a Transition Point.....	1500
Note: A Non-Spattering Wash Bottle.....	1502

### Organic and Biological.

Elliott Quincy Adams: Relations between the Constants of Dibasic Acids and of Amphoteric Electrolytes.....	1503
F. B. Dains, H. R. O'Brien and C. L. Johnson: On the Reactions of the Formamides. V. On Some Pyrazolone Derivatives.....	1510
Dorothy A. Hahn: The Reactions of Some Carboxyl Derivatives of Trimethylene.....	1517
Hilton Ira Jones and Alfred N. Cook: The Mononitro Phenyl Ethers.....	1534
Treat B. Johnson and E. Heaton Hemingway: Researches on Thiocyanates and Isothiocyanates. IX. Ethyl Isothiocyanacetate.....	1550
Treat B. Johnson and A. Willard Joyce: Researches on Pyrimidines. LXXX. The Mechanism of the Action of Bromine on 2-Mercaptopyrimidines.....	1557
C. S. Hudson: Some Numerical Relations among the Rotatory Powers of the Compound Sugars.....	1566
C. S. Hudson and E. Yanovsky: The Isomeric Alpha and Beta Hexacetates of $\alpha$ -Glucoheptose.....	1575
M. Gomberg and N. E. Van Stone: Triphenylmethyl. XXVI. Tautomerism of Triarylcarbinols.....	1577
Marston Taylor Bogert and George Scatchard: Researches on Quinazolines. XXXIII. A New and Sensitive Indicator for Acidimetry and Alkalimetry, and for the Determination of Hydrogen-ion Concentrations between the Limits of 6 and 8 on the Sorensen Scale.....	1606
Walter G. Karr and Howard B. Lewis: A Comparative Study of the Distribution of Urea in the Blood and Tissues of Certain Vertebrates with Especial Reference to the Hen.....	1615
J. H. Long and Mary Hull: On the Assumed Destruction of Trypsin by Pepsin and Acid.....	1620
H. C. Sherman and A. P. Tanberg: Experiments upon the Amylase of <i>Aspergillus Oryzae</i> .....	1638
Correction.....	1645
New Book: Qualitative Analysis.....	1645

## September.

### General, Physical and Inorganic.

F. E. Wright: The Petrographic Microscope in Analysis.....	1647
T. W. Richards and C. Wadsworth, 3d.: Density of Radio-Lead from Pure Norwegian Cleveite.....	1658
Eugene P. Schoch and Denton J. Brown: An Electro-Analytical Method for the Determination and Separation of the Metals of the Copper-Tin Group...	1660
E. P. Schoch and F. M. Crawford: The Electroanalysis of Silver with Solutions of Silver Chloride in Ammonia.....	1682
B. S. Davisson: Titrametric Determination of Nitrites.....	1683
J. W. Shipley: Sodium Pyrogallate as a Reagent for the Determination of Oxygen	1687
Philip L. Blumenthal and S. D. Averitt: The Estimation of Thiosulfate Sulfur in Lime-Sulfur Solutions by Iodine Titration.....	1701
A. R. Middleton and H. L. Miller: Detection of Nickel in Cobalt Salts.....	1705
Note: An Apparatus for Determining the Ions in a Solution.....	1711

## Organic and Biological.

James Kendall and James Eliot Booge: Studies on Catalysis. I. The Addition Compounds of Esters with Organic Acids.....	1712
Julius Stieglitz and Helen Tredway Graham: The Thermal Decomposition of Symmetrical Diarylhydrazines.....	1736
W. H. Hunter, A. O. Olson and E. A. Daniels: A Catalytic Decomposition of Certain Phenol Silver Salts.....	1761
J. R. Bailey and L. A. Mikeska: Hydrazino Diacids.....	1771
LeRoy McMaster and A. C. Magill: The Neutral Ammonium Salts of Some Organic Acids and their Substituted Derivatives.....	1785
N. C. Qua and D. McLaren: The Action of a Solution of Potassium Hydroxide in Alcohol on Oxalic Esters.....	1803
Rasik Lal Datta and Francis Vito Fernandes: Halogenation. XI. Chlorination with Aqua Regia. The Chlorination of Hydrocarbons.....	1809
Rasik Lal Datta and Nihar Ranjan Chatterjee: Halogenation. XII. The Formation of Chloropicrin and Tetrachloroquinone by the Action of Aqua Regia on Organic Substances.....	1813
Marguerite Wilcox and Roger F. Brunel: The Reversible Replacement of Alcohols in Aldehydealcoholates.....	1821
F. B. Dains and A. E. Stephenson: On the Reactions of the Formamides. VI. Some Thiazole Derivatives.....	1841
Treat B. Johnson and Sidney E. Hadley: Researches on Pyrimidines. LXXXI. Secondary-Pyrimidine-Nucleosides and their Unique Behavior on Hydrolysis.....	1844
Treat B. Johnson and A. Willard Joyce: Researches on Pyrimidines. LXXXII. The Synthesis of 1,3-Diamines by Reduction of 2-Mercapto-6-oxypyrimidines.....	1854
Treat B. Johnson and E. Heaton Hemingway: Researches on Thiocyanates and Isothiocyanates. X. The Utilization of Tetrachloromethylmercaptan for the Preparation of Alkyl Isothiocyanates.....	1860
C. S. Hudson and Ralph Sayre: The Optical Rotatory Powers of Some Acetylated Derivatives of Maltose, Cellose and Lactose.....	1867
A. W. Homberger and J. C. Munch: The Quantitative Determination of Morphine in the Various Organs when Injected into Cats and Rabbits.....	1873
H. C. Sherman and P. W. Punnett: On the Products of the Action of Certain Amylases upon Soluble Starch, with Special Reference to the Formation of Glucose.....	1877
H. C. Sherman and J. C. Baker: Experiments upon Starch as Substrate for Enzyme Action.....	1885
Corrections.....	1904
New Books: Practical Physical Chemistry; A Laboratory Course in Organic and Physiological Chemistry.....	1905

## October.

## General, Physical and Inorganic.

J. C. W. Frazer and R. T. Myrick: The Osmotic Pressure of Sucrose Solutions at 30°.....	1907
Harry Shipley Fry and Joseph L. Donnelly: Reactions in Non-aqueous Solvents. I. The Action of Chromyl Chloride upon the Phosphorus Trihalides.....	1923
Eugene P. Schoch and William A. Felsing: The Influence of the Potassium Ion and of the Calcium Ion upon the Ferri-Ferrocyanide Potential.....	1928

S. W. Young and Allen Edwin Stearn: The Basic Copper Sulfates.....	1947
F. W. Bruckmiller: Chlorides in Presence of Thiocyanates.....	1953
James H. Walton and DeWitt O. Jones: The Catalytic Decomposition of Hydrogen Peroxide in Certain Nonaqueous Solutions.....	1956
Marks Neidle and Jacob Barab: Studies in Dialysis. I. The Dialysis of a Colloidal Solution of Hydrous Chromic Oxide in Chromic Chloride.....	1961
Harry N. Holmes and R. E. Rindfusz: The Colloidal Arsenates and Phosphates of Iron.....	1970
John Arthur Wilson: Theory of Colloids:.....	1982
Herbert S. Harned: The Hydrogen and Chlorine Ion Activities of Solutions of Potassium Chloride in 0.1 Molal Hydrochloric Acid.....	1986
S. B. Kuzirian: Estimation of Calcium in Ash of Forage Plants and Animal Carcasses.....	1996
H. C. P. Weber and H. A. Winkelmann: A Systematic Separation of the Anions of Group I. Anions whose Silver Salts are Insoluble in Nitric Acid.....	2000
G. Ennis Smith: Lead Arsenates.....	2014
C. C. McDonnell and C. M. Smith: The Arsenates of Lead.....	2027
Gregory P. Baxter and Howard W. Starkweather: The Efficiency of Calcium Chloride. Sodium Hydroxide and Potassium Hydroxide as Drying Agents	2038
Notes.....	2042

## Organic and Biological.

Julius Stieglitz and Bert Allen Stagner: Molecular Rearrangements of $\beta$ -Triphenylmethyl- $\beta$ -methyl Hydroxylamines and the Theory of Molecular Rearrangements.....	2046
Bert Allen Stagner: The Molecular Rearrangement of Triarylmethylhydroxylamines.....	2069
Isabella Vosburgh: The Molecular Rearrangement of Triphenylmethylhalogenamines.....	2081
Agnes Fay Morgan: The Molecular Rearrangement of Some Triarylmethylchloroamines.....	2095
W. R. Orndorff and C. C. Rose: Diethylamino- <i>m</i> -hydroxybenzoyltetrachlorobenzoic Acid and Trichlorodiethylaminoxanthonecarboxylic Acid and Some of their Derivatives.....	2101
G. D. Van Epps and E. Emmet Reid: Studies in the Preparation of Nitriles. II. The Preparation of Aliphatic Nitriles.....	2120
G. D. Van Epps and E. Emmet Reid: Studies in the Preparation of Nitriles. III. The Catalytic Preparation of Nitriles.....	2128
Treat B. Johnson and George C. Bailey: Researches on Amines. V. The Structure of Vitiatine. Synthesis of Methylethylenediamine.....	2135
Bessie M. Brown and S. F. Acree: On the Reaction of Both the Ions and the Nonionized Forms of Acids, Bases and Salts: The Reaction of Methyl Iodide and Sodium, Potassium and Lithium Ethylates at 0°.....	2145
Arthur W. Dox and G. P. Plaisance: A Comparison of Barbituric Acid, Thiobarbituric Acid and Malonylguanidine as Quantitative Precipitants for Furfural.....	2156
Arthur W. Dox and G. P. Plaisance: Condensation of Thiobarbituric Acid with Aromatic Aldehydes.....	2164
W. O. Emery and S. Palkin: Researches on Organic Periodides.....	2166
Francis C. Krauskopf and George Ritter: The Colors Produced by Resorcinol in Solutions of Certain Salts and the Use of these Colors as a Means of Detecting Resorcinol in the Presence of Other Phenols.....	2182



J. K. Dale: Preparation of Bromoacetylglucose and Certain Other Bromoacetyl Sugars.....	2187
Hiizu Ito: Quantitative Determinations of Hippuric Acid in Urine, Blood, Muscles and Liver. A Method.....	2188
J. J. Willaman: Modification of the Pratt Method for the Determination of Citric Acid.....	2193
H. C. Sherman and Dora E. Neun: An Examination of Certain Methods for the Study of Proteolytic Action.....	2199
Correction.....	2216
New Book: A System of Physical Chemistry.....	2217

## November.

### General, Physical and Inorganic.

Annual Report of the International Committee on Atomic Weights, 1917.....	2219
Irving Langmuir: The Constitution and Fundamental Properties of Solids and Liquids.....	2221
Hugh Stott Taylor: The Thermodynamic Properties of Silver and Lead Iodides..	2295
N. Edward Loomis and Merle R. Meacham: A Study of the Tenth-Normal Hydrochloric Acid Calomel Electrode.....	2310
B. B. Wroth and E. Emmet Reid: The Solubilities of Liquids in Liquids. The Partition of the Lower Alcohols between Water and Cottonseed Oil.....	2316
Samuel Palkin: The Separation of Lithium from the Other Alkali Metals.....	2326
B. Smith Hopkins and Clarence W. Balke: The Purification and Atomic Weight of Yttrium.....	2332
Gilbert N. Lewis and Merle Randall: The Free Energy of Bromine Compounds.	2348
G. A. Linhart: The Potential of the Mercury Electrode against Mercurous Ion..	2356
Paul H. M.-P. Brinton: The Vanadates of Beryllium.....	2361
C. C. McDonnell and C. M. Smith: The Arsenates of Lead.....	2366
Graham Edgar: The Reduction of Vanadic Acid by Hydriodic Acid.....	2369
Orland R. Sweeney: Analysis of Certain Tungsten Derivatives.....	2377
J. Bennett Hill: New Derivatives of Tungsten.....	2383
N. Edward Loomis and S. F. Acree: The Effect of Pressure upon the Potential of the Hydrogen Electrode.....	2391
W. A. Taylor and S. F. Acree: Studies in the Measurement of the Electrical Conductivity of Solutions at Different Frequencies. V. Investigations on the Use of the Vreeland Oscillator and Other Sources of Current for Conductivity Measurements.....	2396
W. A. Taylor and S. F. Acree: Studies in the Measurement of the Electrical Conductivity of Solutions at Different Frequencies. VI. Investigations on Bridge Methods, Resistances, Cells, Capacities, Inductances, Phase Relations, Precision of Measurements, and a Comparison of the Resistances Obtained by the Use of Inductance and Capacity Bridges.....	2403
W. A. Taylor and S. F. Acree: Studies in the Measurements of the Electrical Conductivity of Solutions at Different Frequencies. VII. Investigations of the True and Apparent Resistances, Voltage, Apparent Capacity, Size and Character of Electrodes, Ratio of Inductance Changes to Resistance Changes, and the Relation of Induction and Capacity to Frequency.....	2415
Edward W. Washburn: The Measurement of Electrolytic Conductivity. I. The Theory of the Design of Conductivity Cells.....	2431
James Kendall: Review: The Preparation of Conductivity Water.....	2460

## Organic and Biological.

Gerald E. K. J. : The Hydrolysis of Hexahydropyrimidine.....	2466
G. H. Woolf : The Silver Salt of Triiodophenol and its Catalytic Decompositions.....	2474
C. G. Derick and D. W. Bissell: Studies of Trimethylene Oxide.....	2478
W. R. Orndorff and J. J. Kennedy: The Nitration Products of Phenoltetrachlorophthalein and Some of their Derivatives.....	2486
R. S. Bochner and C. E. Andrews: The Pyrogenetic Decomposition of Amides. I.....	2503
R. S. Bochner and A. L. Ward: The Pyrogenetic Decomposition of Amides. II.....	2505
Norman A. Shepard: Researches on Amines. VI. The Utilization of Hypochlorite Color Reactions in Establishing the Mechanism of the Action of Dimethylsulfate on Aniline.....	2507
Roger Adams and L. F. Weeks: Action of Oxalyl Chloride on Primary, Secondary and Tertiary Alcohols.....	2514
F. D. Chattaway: The Crystallization of Calcium Tartrate.....	2519
J. R. Bailey and A. T. McPherson: The 5,5-Dimethyl-3-R-2-Thiohydantoin.....	2523
Ralph C. Huston and Theodore E. Friedemann: Action of Aromatic Alcohols on Aromatic Compounds in the Presence of Aluminium Chloride. I.....	2527
Marguerite Willcox and Roger F. Brunel: The Molecular Weight of Some Alcohols of Chloral and Butylchloral in Benzene Solution.....	2533
William J. Hale: Studies in the Cyclopentadiene Series. IV. The Formation of Cyclopentadienodihydropyridazines.....	2535
Rasik Lal Datta and Nihar Ranjan Chatterjee: Halogenation. XIV. Bromination of Hydrocarbons by Means of Bromine and Nitric Acid.....	2545
W. C. Cope and J. Barab: Application of the Nitrometer for the Determination of Constitution and Estimation of Nitrogen in a Class of Nitrocompounds. (Nitroamines).....	2552
Burt E. Nelson: The Composition of Neurokeratin.....	2558
Arthur W. Dox and A. E. Lamb: An Accurate Aeration Method for the Determination of Alcohol in Fermentation Mixtures.....	2561
Philip Adolph Kober: The Efficiency of the Aeration Method for Distilling Ammonia; In Answer to Certain Criticisms.....	2568
P. A. Bonquet: Presence of Nitrites and Ammonia in Diseased Plants.....	2572
New Book: Annual Reports of the Progress of Chemistry for 1915.....	2576

## December.

## General, Physical and Inorganic.

Donald P. Smith and Frederick H. Martin: The Occlusion of Hydrogen by a Palladium Cathode.....	2577
Frederick H. Getman: The Action of Magnesium on Solutions of Potassium Chloride.....	2594
Marks Neidle and John N. Crombie: Oxidation-Reduction Reactions without the Addition of Acid.....	2607
Theodore W. Richards and Charles Wadsworth, 3d: Further Study of the Atomic Weight of Lead of Radioactive Origin.....	2613
Louis J. Curtman and Ben R. Harris: The Systematic Detection of Thiocyanates.....	2622
James M. Bell: Free Energy and Heat Capacity.....	2629
Herbert F. Sill: The Influence of Pressure on Solubility.....	2632

William D. Harkins, R. E. Hall and W. A. Roberts: Studies on the Cobalt-ammines. I.....	2643
Ralph E. Hall and William D. Harkins: The Free Energy of Dilution and the Freezing-Point Lowerings in Solutions of Some Salts of Various Types of Ionization, and of Salt Mixtures.....	2658
William D. Harkins and W. A. Roberts: The Freezing-Point Lowerings in Aqueous Solutions of Salts and Mixtures of Salts and of a Salt with a Nonelectrolyte.....	2676
William D. Harkins and W. Tudor Pearce: Ionization and Solubility Relations of Salts of Higher Types. IV.....	2679
William D. Harkins and Harry M. Paine: The Effect of Salts upon the Solubility of Other Salts. VIIIa. The Solubility Relations of a Very Soluble Bi-Univalent Salt.....	2709
William D. Harkins and W. Tudor Pearce: The Effect of Salts upon the Solubility of Other Salts. VIIIb. The Solubility Relations of Some Extremely Soluble Salts.....	2714
James Kuhn Senior: The Molecular Rearrangement of Triarylmethylazides....	2718
Julius Stieglitz and James Kuhn Senior: The Molecular Rearrangement of <i>sym-bis</i> -Triarylmethylhydrazines. Preliminary Report.....	2727

## Organic and Biological.

Rasik Lal Datta and Jogendra Kumar Choudhury: Halogenation. XIII. Methods of Estimation of Semicarbazide, Semioxamizide and Oxalyldrazide by their Interactions with Halogens and Halogen Oxyacids.....	2736
T. B. Aldrich and C. P. Beckwith: Studies on Derivatives of Trihalogentertiary-Butyl-Alcohols.....	2740
J. H. Sachs and E. Emmet Reid: Studies in Esterification. VII.....	2746
J. W. Kimball and E. Emmet Reid: Studies in Esterification. VIII.....	2757
Roger Adams and C. H. Beebe: Action of the Grignard Reagent on CN Compounds. Synthesis of Amidines from Cyanamides.....	2768
H. A. Lubs and S. F. Acree: On the Sulfonphthalein Series of Indicators and the Quinone-Phenolate Theory.....	2772
George D. Beal and Fred Weaver Muncie: Effects of Large Applications of Commercial Fertilizers on Carnations.....	2784
Merrill C. Hart and Frederick W. Heyl: Some Constituents of Jambul.....	2805
New Books: Laboratory Manual of Inorganic Chemistry for Colleges; Elementary Qualitative Analysis.....	2813



"Crisco" cooking oil, well stirred in a large beaker, was employed as a bath. A Bunsen burner was regulated to maintain a temperature one or two degrees below that desired, and the final temperature was obtained from an elongated electric light bulb partially immersed in the bath. With a switch to operate this light, the temperature of the bath could easily be maintained constant, to within a few hundredths of a degree, at any desired point from that of the room to about  $200^{\circ}$ . The mercury thermometer used was a standard instrument, graduated to  $1/5^{\circ} C.$ , and calibrated by the Reichsanstalt. A correction was applied for the exposed stem.

The saturation temperature was taken as the mean of determinations made with rising and falling temperatures.<sup>1</sup> For the former, the temperature was first raised sufficiently to completely dissolve the ammonium bromide. By sudden cooling very small crystals were obtained which dissolved sharply when the bulb was placed in the bath and the temperature was gradually raised. The supporting handle of the bulb was constantly tapped, giving the contents an irregular rotary motion, to assist in the rapid attainment of equilibrium. In order to make the disappearance of the crystals, as well as their formation in the following determination, as distinct as possible, the bath was illuminated by a strong electric light placed directly behind it. The crystallization temperature was determined by allowing all but one or two small fragments of the crystals to dissolve. By then allowing the temperature of the bath to fall gradually, the point at which crystallization became noticeable was determined. The difference between the two temperatures determined in this way varied from  $0.2^{\circ}$  to  $0.6^{\circ}$ . Their mean, the accuracy of which was within  $\pm 0.2^{\circ}$ , was taken as the equilibrium temperature for saturation.

#### Calculation of the Weight of Water in the Vapor Phase.

At temperatures below  $60^{\circ}$ , where the volume of the gas space is of the order of 1 cc., as in the present case, no correction for the weight of water in the vapor phase was needed. Above  $60^{\circ}$ , the correction becomes appreciable and at higher temperatures failure to take this factor into consideration may readily introduce an error of 1% or more in the calculation of the composition of the liquid phase.

The volume of each bulb being known, the fraction of the volume occupied by the liquid at the saturation temperature was "estimated" and from this estimated volume and the total weight of the solution, an approximation of its density was obtained. The density estimations at slightly different temperatures were averaged, as were also the temperatures themselves, and the results plotted. In as much as these densities, along with the density of saturated ammonium bromide solution at  $15^{\circ}$ ,<sup>2</sup>

<sup>1</sup> Cf. Hartley, *Loc. cit.*

<sup>2</sup> Eder, *Ibid.*

fall on a fairly smooth curve, the approximation was considered sufficiently close for the purpose. The densities used were:

$t$ .....	$15^{\circ}$	$113^{\circ}$	$137^{\circ}$	$158^{\circ}$
$d$ .....	1.29	1.66	1.71	1.76

The density of the saturated solution read from this curve was then employed to calculate the volume of the liquid phase in any given case and, by subtracting from the total volume of the bulb,<sup>1</sup> the volume of the gas space was obtained.

The vapor pressure of the solution was taken to be the same fraction of the vapor pressure of water, at a given temperature, as the molar fraction of water in the system. This again is only a rough approximation, but sufficiently accurate for the purpose.

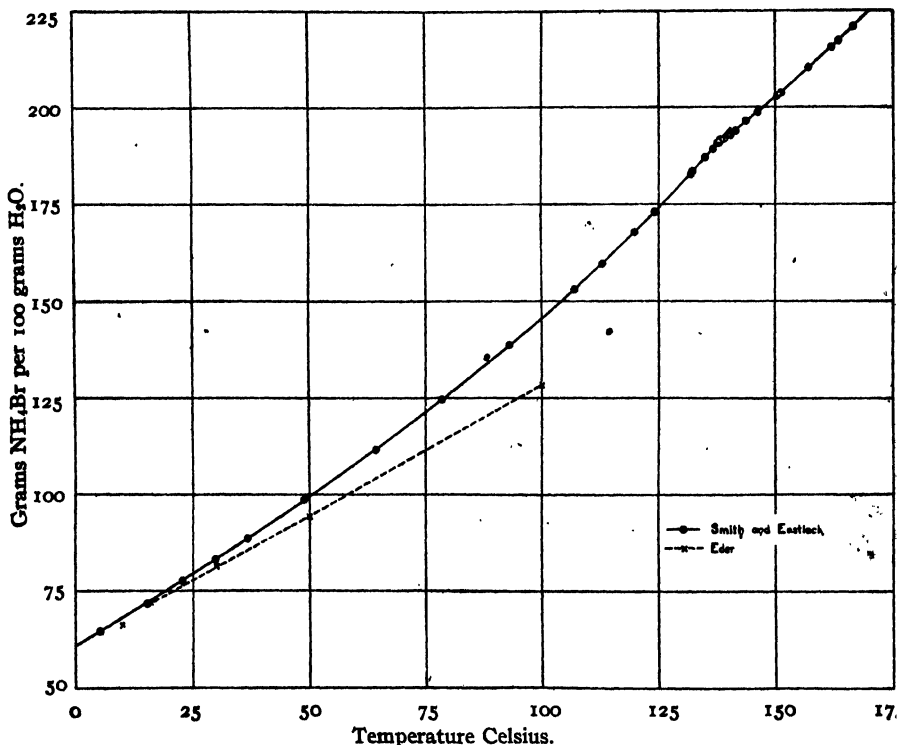


Fig. 2.—The solubilities of ammonium bromide in water.

The weight of water vapor was calculated from its volume and partial pressure as thus obtained, and was subtracted from the total weight of water in the bulb before the composition of the liquid phase was calculated.

<sup>1</sup> The increase in volume of the bulb due to the expansion of the glass was estimated to be negligibly small.

The correction thus applied varied from zero at low temperatures to 0.0019 g. at one of the higher temperatures, out of a total weight of 0.1 to 0.2 g. of water.

### Experimental Results.

The results of the determinations of the solubility of ammonium bromide in water are given in Table I.

TABLE I.—SOLUBILITIES OF NH<sub>4</sub>Br IN H<sub>2</sub>O—OBSERVATIONS.

Weight NH <sub>4</sub> Br.	Weight H <sub>2</sub> O.	Vol. of bulb, cc.	Weight H <sub>2</sub> O vapor (calc.), gram.	Ratio, weight NH <sub>4</sub> Br H <sub>2</sub> O (liquid)	Molar fraction. NH <sub>4</sub> Br.	Temp. of satn.
0.1774	0.2750	..	..	0.6452	0.1061	5.3
0.1570	0.2188	..	..	0.7174	0.1166	15.2
0.1978	0.2549	..	..	0.7762	0.1250	22.7
0.1714	0.2062	..	..	0.8312	0.1326	29.8
0.1987	0.2247	..	..	0.8845	0.1399	36.7
0.2327	0.2361	..	..	0.9856	0.1535	48.9
0.2529	0.2268	0.80	0.0001	1.115	0.1702	64.4
0.1788	0.1437	1.12	0.0002	1.247	0.1865	78.6
0.3162	0.2286	1.10	0.0003	1.386	0.2031	93.0
0.2423	0.1591	1.39	0.0007	1.530	0.2195	107.0
0.3162	0.1993	2.12	0.0012	1.596	0.2270	113.0
0.2991	0.1791	1.14	0.0007	1.677	0.2355	119.9
0.3036	0.1762	1.0	0.0007	1.730	0.2414	124.1
0.2629	0.1445	0.72	0.0005	1.826	0.2514	132.0
0.2072	0.1137	0.81	0.0007	1.833	0.2522	132.3
0.2293	0.1234	0.84	0.0008	1.870	0.2560	135.0
0.3967	0.2105	0.87	0.0007	1.891	0.2580	136.7
0.2322	0.1235	0.77	0.0007	1.891	0.2580	136.9
0.2066	0.1092	0.79	0.0008	1.906	0.2595	137.6
0.3197	0.1685	0.93	0.0009	1.907	0.2597	137.9
0.3666*	0.1921	0.90	0.0008	1.916	0.2606	138.2
0.3666	0.1921	0.90	0.0008	1.916	0.2606	139.1
0.3624	0.1889	1.02	0.0010	1.929	0.2619	140.4
0.2971	0.1541	0.85	0.0009	1.939	0.2629	141.5
0.2718	0.1394	0.92	0.0010	1.963	0.2655	143.7
0.3657	0.1852	1.10	0.0013	1.988	0.2677	146.2
0.3512	0.1742	0.94	0.0012	2.030	0.2718	150.4
0.3716	0.1835	0.93	0.0011	2.037	0.2726	151.1
0.3111	0.1495	1.0	0.0015	2.102	0.2788	157.0
0.2913	0.1835	1.13	0.0019	2.155	0.2838	161.9
0.3960	0.1839	1.0	0.0016	2.172	0.2854	163.4
0.4221	0.1926	0.95	0.0016	2.210	0.2890	166.6

\* Same tube as one below. Point on metastable portion of curve. See below.

The points obtained lie on two smooth curves which intersect at 137.3° ± 0.3° (Fig. 2). For convenience of reference the solubilities of ammonium bromide at rounded temperatures up to 100°, as read from the carefully smoothed curve plotted on a large scale, are listed in Table II.

TABLE II.—SOLUBILITIES OF  $\text{NH}_4\text{Br}$  IN  $\text{H}_2\text{O}$  TO  $100^\circ$  AT ROUNDED TEMPERATURES.

Temp. °C.	G. $\text{NH}_4\text{Br}$ per 100 g. $\text{H}_2\text{O}$ .	Molar fraction. $\text{NH}_4\text{Br}$ .	Temp. °C.	G. $\text{NH}_4\text{Br}$ per 100 g. $\text{H}_2\text{O}$ .	Molar fraction. $\text{NH}_4\text{Br}$ .
0	60.6	0.1004	40	91.1	0.1437
5	64.3	0.1058	45	95.2	0.1491
10	68.0	0.1112	50	99.2	0.1546
15	71.7	0.1165	60	107.8	0.1656
20	75.5	0.1220	70	116.8	0.1768
25	79.3	0.1274	80	126.0	0.1881
30	83.2	0.1328	90	135.6	0.1996
35	87.1	0.1383	100	145.6	0.2111

In one instance (Experiment marked \* Table I) a point on the meta-stable portion of the lower solubility curve was obtained. This was accomplished by placing the cold tube in the bath maintained at the temperature predicted by prolongation of the lower curve and the known composition of the contents of the bulb. In this manner it was possible to completely dissolve the crystals at a temperature nearly  $1^\circ$  below that at which the same sample, when in the form stable at that temperature, was found to dissolve. In order to determine the saturation temperature for the stable form, the temperature of the bath was raised a degree or so above the transition point and the solid was allowed to stand several minutes in contact with the solution (without shaking). On lowering the temperature slightly and determining the saturation temperature in the usual manner the point on the equilibrium curve was obtained.

The solubilities from 0 to  $100^\circ$  do not agree with those given by Eder. To show the amount of the discrepancy, his values are plotted with our own results in Fig. 2. He gives no description of his method of determining the solubility.

### Summary.

Heating and cooling curves showed the transition point of ammonium bromide to lie between  $130^\circ$  and  $143^\circ$ . The solubilities in water from 0 to  $170^\circ$  were determined by the closed tube method. A well defined break in the solubility curve occurs at  $137.3^\circ$ , the transition temperature. The solubility measurements from 0 to  $100^\circ$  do not agree with the only ones heretofore available in the literature.

NICHOLS LABORATORIES OF INORGANIC CHEMISTRY,  
COLUMBIA UNIVERSITY, NEW YORK CITY.

### [CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.] THE PRACTICAL INSTALLATION OF THE DOUBLE COMBINATION POTENTIOMETER.

By MERLE RANDALL, F. RUSSELL v. BICHOWSKY AND W. H. RODEBUSH.

Received April 11, 1916.

The advantages of multiple thermoelements for use in calorimetry, and the design and installation of suitable potentiometers for these and



other precise potential measurements have been discussed at length by White.<sup>1</sup> In attempting to install a double combination potentiometer<sup>2</sup> of highest sensitivity, certain improvements and precautions not discussed by White have been worked out.

Our instrument was originally designed for use with lead storage cells as the primary source of electromotive force. The lead cell is not satisfactory. In the first place the e. m. f. is unnecessarily high, thus increasing leakage difficulties. In the second place the cell has a high temperature coefficient and even at constant temperature the e. m. f. is not particularly constant. Thus the instrument requires frequent comparison with the standard cell. On the other hand, the large size Hulett<sup>3</sup> standard battery is free from these defects, our batteries seldom varying under working conditions by more than 0.0001 volt. However, because the e. m. f. of the Hulett battery is but slightly greater than that of the standard cell, certain changes in the design of the instrument were necessary. These changes affect only the low-resistance side of the instrument. In the original instrument the battery current flowed through both the dial resistances of 99 ohms and an auxiliary resistance of 1018 ohms. This last coil was used not only as an auxiliary resistance, but also for checking the battery current against the standard cell (1.0181 volts at 25°). The Hulett cell does not give a sufficient e. m. f. to force a current of 0.001 amp. through these two resistances. We therefore substituted for the 1018 ohms coil in the battery circuit a coil (W) of 919.1 ohms, making the total resistance of the battery circuit inside the potentiometer 1018.1 ohms. We then re-arranged the connections so that the battery current is checked against the standard cell through this total resistance, and the old coil is used as a substitute resistance when the potentiometer is cut out.

The precise details of the connections as modified will be made clear by reference to Fig. 1 which combines Figs. 7, 10 and 11 of White<sup>4</sup> into a simple schematic diagram. The block letters refer to the same parts as in Fig. 11, and the roman to the letters given to the binding posts by the makers of our instrument. What the significance of this last lettering is we have been unable to ascertain. The heavy lines indicate those parts included in the potentiometer box. In practice switches  $E_1$ ,  $E_2$  and  $E_3$  are combined into a single 3-pole double-throw switch. Similarly, switch M is a 4-pole double-throw and SC and SH are 2-pole double-throw switches. Switches SC and SH correspond to the unlettered switches of White, Fig. 12.

<sup>1</sup> THIS JOURNAL, 36, 1856, 1868, 2011, 2292, 2313 (1914).

<sup>2</sup> Leeds and Northrup Instrument No. 26761.

<sup>3</sup> *Phys. Rev.*, 27, 33 (1908).

<sup>4</sup> THIS JOURNAL, 36, 1868 (1914).

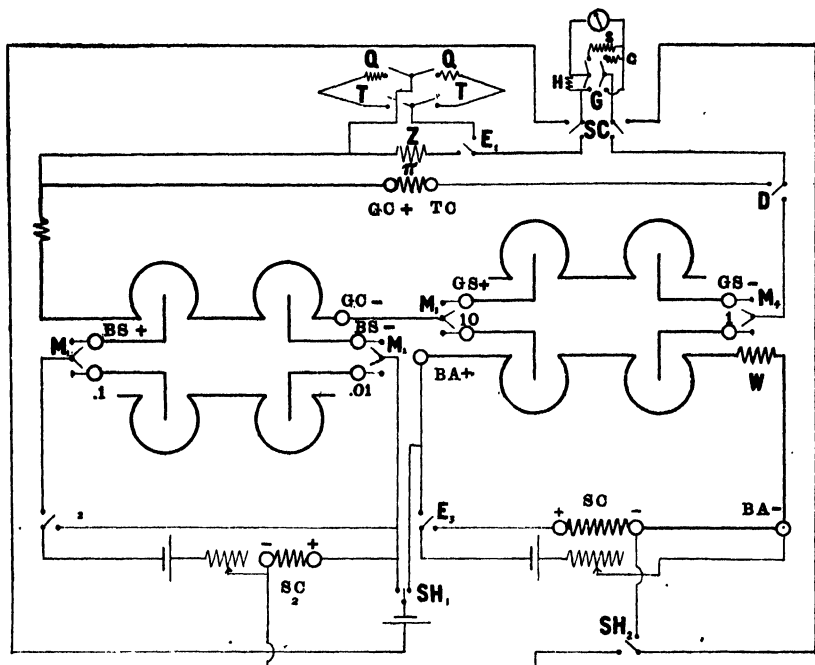


Fig. 1.

**The Elimination of Parasitic Thermoelectric Effects.**—In our installation parasitic thermoelectric effects have been reduced to less than 0.01 microvolt; in fact none are detectable within the limits of sensibility of the galvanometer. This result has been obtained by carefully eliminating all metals except copper in the external circuits, and by entirely enclosing the instrument, wiring and galvanometer.

The special switches which White recommends have been improved by specifying copper instead of brass clips for fastening the wire to the switch contacts, thus providing a continuous copper circuit. It is, of course, unnecessary, and in fact undesirable from a mechanical standpoint, that the screws, bolts, etc., be of copper.

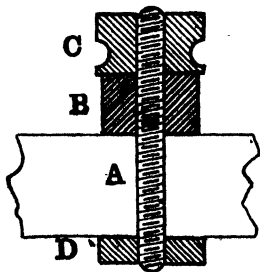


Fig. 2.

While the "clothes-pin" contact of White is entirely satisfactory, we have found the form of binding post shown in Fig. 2 to be more rugged and convenient for a permanent installation. It consists of a threaded copper rod, A, a threaded copper bushing, B, a brass binding nut, C, and a brass nut, D, soldered to the copper rod. The permanent connection is made by soldering to the copper rod. This binding post is much cheaper than an all copper post, is thermoelectrically as satisfactory, and mechanically much better.

The remaining thermal parasitics are mainly in the brass binding posts of the galvanometer and potentiometer box. These brass binding posts should be replaced by posts of the type described in the preceding paragraph. In our instrument we have not made these replacements but have eliminated these effects by complete thermal enclosure.

**Insulation.**—For an instrument that is to be used in a chemical laboratory it is essential that there be as few exposed electrical parts as possible, and that the insulation between different exposed parts be of such a nature that it can easily be renewed. Properly treated paraffin forms a most satisfactory insulation. In our instrument all the wires are led through glass tubes which are embedded in paraffin. The paraffin used for purposes of insulation should be of the best quantity obtainable, should be boiled before using, and should be cast in thin layers, each of which is allowed to harden before a successive one is applied. Paraffin thus treated has an effective resistance of more than  $10^{11}$  ohms per cm./cm<sup>2</sup>. The complete enclosure of all of the wires in one solid block of paraffin makes local electrical shielding almost unnecessary. The whole instrument, galvanometer, and connected apparatus must, of course, be shielded by White's method. In many cases where the insulation is not perfect we have found local shielding a positive disadvantage.<sup>1</sup> The switches should be particularly well insulated. We have replaced the fiber parts by bakelite and have submerged the bases entirely in paraffin, thus allowing a renewal of the surface insulation from time to time.

For convenience our instrument is mounted as a unit upon a wooden table 36" × 36". The Hulett batteries are carried on a shelf below the table. All the wiring is brought underneath the table through glass, paraffin-filled tubes, and the connections cast as a unit in a shielded paraffin block. Following the suggestion of White, the various switches, rheostats, and resistances are mounted in a tin-lined wooden box and operated by draw rods. It is of great advantage to enclose the sliding contacts on the top of the potentiometer box and to operate the dials by means of shielded extension handles. Connections to the standard cell, batteries, galvanometer and thermoelements are made by means of copper binding posts outside the enclosing case.

We have found the unprotected galvanometer the source of very serious thermoelectric forces. At the suggestion of Prof. Lewis it was enclosed in a heavy sheet copper box with a small plane glass window. The box is connected with the shielding system. The telescope is mounted on the top of the case enclosing the switches 50 cm. from the galvanometer mirror and the strongly illuminated scale is several meters away and at such a height that troublesome double reflections are avoided. The galvanometer switches are operated by foot pedals.

<sup>1</sup> Leakage currents may best be tested for by short-circuiting the thermocouple.

**The Galvanometer.**—For use with multiple thermoelements of 20 to 50 couples a galvanometer of the following specifications<sup>1</sup> is recommended: resistance 30 ohms, external critical damping resistance 400 ohms, period 7 sec., sensitivity 4 mm. per microvolt with the damping resistance in series. The potentiometer is usually used with several thermocouples which have different resistances. Instead of changing  $Z$  (Fig. 1) to correspond to the resistance of each thermocouple, it is fixed at 400 (C. D. R. of galvanometer)—105.5 (resistance of remainder of external galvanometer circuit) and an auxiliary resistance,  $Q$ , placed in series with each thermocouple. This resistance  $Q$  is wound of copper wire so as to be free of thermoelectric forces, and has such a value that its resistance added to that of the thermocouple equals  $Z$ .

For the above galvanometer the resistance  $S$  should have the value 400 ohms, and  $H$  3572 ohms<sup>2</sup> in order that the galvanometer can be set to give  $1/10$  sensitivity.

Our instrument as finally set up has no detectable thermoelectric parasitics, and only an extremely constant leakage e. m. f. of slightly less than 0.1 microvolt.

BERKELEY, CAL.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF PITTSBURGH, PITTSBURGH, PA.]

## THE TEMPERATURE EFFECT IN DIALYSIS AND A SIMPLE RAPID DIALYZER.<sup>3</sup>

By MARKS NEIDLE.

Received April 27, 1916.

The speed of dialysis depends upon the following factors: First, the nature of the membrane; second, the area of the membrane which is in contact with liquid on both sides; third, the difference in concentration of diffusible substances in internal and external liquids close to the membrane; fourth, the temperatures of the internal and external liquids.

By utilizing, especially the third and fourth principles, it is possible to prepare large quantities of inorganic hydrosols, containing only minute amounts of electrolytes, in a comparatively short time. The method consists in suspending a parchment paper membrane of about one liter capacity in a two liter beaker containing about a liter of the solution to be dialyzed. Distilled water is run at a fairly constant rate into the membrane, which is maintained a little more than half full by means of an automatic syphon. The colloidal solution which is in the beaker is heated to any desired temperature (70–90°).

<sup>1</sup> For use with low-resistance couples the critical damping resistance can be reduced to 150 ohms with an increase of sensitivity.

<sup>2</sup> For a galvanometer 150 ohms C. D. R.,  $S = 150$  ohms, and  $H = 1625$  ohms.

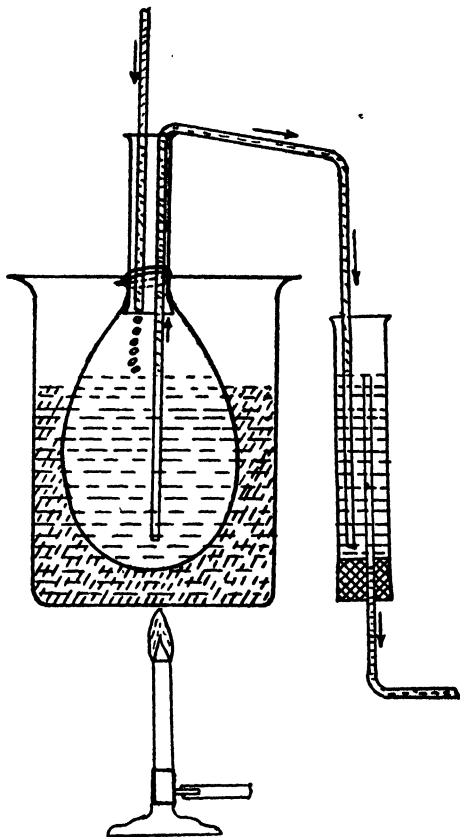
<sup>3</sup> Presented at the spring meeting of the American Chemical Society, 1916.

Wobbe<sup>1</sup> and Nicolardot<sup>2</sup> speak of a process of hot dialysis but they neither describe their methods nor discuss the advantages of dialyzing in this way. In connection with a device, which is essentially a modified Soxhlet apparatus, for the quantitative and rapid dialysis of small volumes of colloidal solutions, Golodetz<sup>3</sup> mentions that the dialysis membrane which is above the boiling flask is heated to about 40° to 50°, this being favorable to rapid dialysis.

Beyond these mere statements it seems that the temperature effect in dialysis has been completely neglected. Its importance is evident from the fact that the simple apparatus represented in the diagram gives in twenty days a hydrous ferric oxide hydrosol, as pure as, if not purer, than the same hydrosol prepared by dialysis in the cold for six months. A colloidal solution satisfactory for most purposes may be obtained in eight to ten days, while the usual method requires about a month.

The temperature effect becomes apparent as soon as we regard the colloidal solution as a two-phase system in which the electrolyte is distributed between the disperse phase and the dispersion medium according to the laws of adsorption. If the dialyzing membrane is impermeable to the disperse phase, only the electrolyte which is not adsorbed can diffuse directly. Now, if the colloidal solution is heated, this portion of the electrolyte will diffuse more rapidly through the membrane and since the diffusion coefficient<sup>4</sup> increases about 2% per degree, the effect of a temperature increase of 50–70° will be very considerable.

As the electrolyte in the dispersion medium diffuses through the mem-



<sup>1</sup> *Pharm. Centr., H.*, 40, 793 (1899).

<sup>2</sup> *Ann. chim. phys.*, 366, 348 (1905).

<sup>3</sup> *Z. physiol. Chem.*, 86, 315–24 (1913).

<sup>4</sup> Nernst, *Theoretische Chemie*, 7th ed., p. 400.

brane, the equilibrium of distribution of the electrolyte is disturbed, and part of the adsorbed electrolyte diffuses into the dispersion medium from which it can now dialyze. Heating accelerates the re-establishment of equilibrium and consequently hastens dialysis.

Furthermore, in general, adsorption decreases<sup>1</sup> considerably with rise in temperature. For a given total concentration of electrolyte in a colloidal solution at equilibrium there will be more of it in the dispersion medium if the solution is heated, and since diffusion through the membrane depends only on the concentration of the electrolyte in the dispersion medium, heating should be favorable to rapid dialysis.

By placing the solution to be dialyzed in the outside vessel (the beaker) and heating, the large increase in volume due to osmosis, which results in the usual procedure, is avoided. An equilibrium sets in between evaporation from the colloidal solution and osmosis of water into it through the membrane, and the volume remains practically constant. Or, if desired, the solution may be concentrated during dialysis.

The steady flow of distilled water inside the dialyzer helps dialysis by maintaining a maximum difference of concentration of diffusible substances on both sides of the membrane, and also by maintaining within the latter a lower temperature than outside, which introduces the Soret<sup>2</sup> phenomenon.

Our experience is that parchment paper membranes of about one liter capacity are far easier to prepare than collodion membranes of the same size. They stand rough usage, a temperature of over 90° for a long period, and cost very little.

PITTSBURGH, PA.

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## ON THE EQUILIBRIA OF MERCURIC CHLORIDE WITH OTHER CHLORIDES.

By G. A. LINHART.

Received March 6, 1916.

In a recent paper<sup>3</sup> it is shown that the association of mercuric chloride in water solution depends both on the concentration and the temperature, and that the degree of association ranges, in saturated solutions, from 6% at 0° to 58% at 100°. It is, therefore, not surprising that in the absence of these data, previous investigators were not able to account for the abnormal behavior of mercuric chloride in water solution with reference to its molecular weight, distribution ratio, and solubility. Of particular interest are the attempts made by several investigators to establish the type or types of complex compounds which mercuric chloride

<sup>1</sup> *Freundlich Kapillarchemie*, 169-173.

<sup>2</sup> Nernst, *Theoretische Chemie*, 7th ed., p. 801.

<sup>3</sup> *THIS JOURNAL*, 37, 258 (1915).

forms with other chlorides in solution. The results were, of course, entirely unsatisfactory as is evident from the polemics that followed.<sup>1</sup> It is the purpose of this paper to harmonize these opposing views, which resulted partly from the use of unreliable methods of analyses, but chiefly from not taking into account the formation of the double molecules of mercuric chloride in solution.

It has been shown fairly conclusively<sup>2</sup> that in a water solution of mercuric chloride there are two types of molecules,  $\text{HgCl}_2$  and  $\text{Hg}_2\text{Cl}_4$ , which combine to form complex compounds with sodium chloride in water solution, and it only remains to establish, if possible, the type or types of these complexes.

Assuming *only* those complexes which have been isolated<sup>3</sup> from water solutions in definite crystalline forms and of definite chemical composition, then the reactions between the chloride ions of the sodium chloride and the two kinds of molecules of mercuric chloride may be represented by the equations

(a),  $(\text{HgCl}_2) + (\text{Cl})^- \rightleftharpoons (\text{HgCl}_3)^-$ ; (b),  $(\text{Hg}_2\text{Cl}_4) + (\text{Cl})^- \rightleftharpoons (\text{Hg}_2\text{Cl}_5)^-$  when the mercuric chloride is in excess, and by

(c),  $(\text{HgCl}_3)^- + (\text{Cl})^- \rightleftharpoons (\text{HgCl}_4)^{--}$ ; (d),  $(\text{Hg}_2\text{Cl}_5)^- + (\text{Cl})^- \rightleftharpoons (\text{Hg}_2\text{Cl}_6)^{--}$ ; (e),  $(\text{Hg}_2\text{Cl}_6)^{--} + (\text{Cl})^- \rightleftharpoons (\text{HgCl}_3)^- + (\text{HgCl}_4)^{--}$  when the sodium chloride is in large excess.

It is evident that in any concentration of the reacting substances the total concentration of the sodium chloride and the mercuric chloride may be expressed by the sums

$$(\text{HgCl}_2) + (2\text{Hg}_2\text{Cl}_4) + \frac{(\text{HgCl}_3)^-}{\gamma} + \frac{(\text{HgCl}_4)^{--}}{\gamma^2} + \frac{(2\text{Hg}_2\text{Cl}_5)^-}{\gamma} + \frac{(2\text{Hg}_2\text{Cl}_6)^{--}}{\gamma^2} = \Sigma \text{HgCl}_2.$$

$$\frac{(\text{HgCl}_3)^-}{\gamma} + \frac{(2\text{HgCl}_4)^{--}}{\gamma^2} + \frac{(\text{Hg}_2\text{Cl}_5)^-}{\gamma} + \frac{(2\text{Hg}_2\text{Cl}_6)^{--}}{\gamma^2} + \frac{(\text{Cl})^-}{\gamma} = \Sigma \text{NaCl}.$$

<sup>1</sup> Sand and Breest, *Z. physik. Chem.*, **59**, 426 (1907); **60**, 237 (1907); Sherrill, *Z. Elektrochem.*, **9**, 549 (1903); *Z. physik. Chem.*, **43**, 705 (1903); **47**, 103 (1904).

<sup>2</sup> THIS JOURNAL, **37**, 271 (1915).

<sup>3</sup> It is interesting to note that by saturating concentrated aqueous hydrochloric acid solutions with mercuric chloride and cooling to incipient crystallization Ditte obtained compounds of the following composition:

Substance.	60°.	30°.	15°.	5°.	-10°.
$\text{HgCl}_2$ .....	86.58%	82.30%	78.97%	67.10%	57.60%
$\text{HCl}$ .....	3.86	5.54	5.33	12.04	15.51
$\text{H}_2\text{O}$ .....	9.56	12.16	15.70	20.86	26.88
$\text{HHg}_3\text{Cl}_7.5\text{H}_2\text{O}$	$\text{HHg}_3\text{Cl}_8.4\text{H}_2\text{O}$	$\text{HHg}_2\text{Cl}_6.6\text{H}_2\text{O}$	$\text{H}_2\text{Hg}_2\text{Cl}_6.7\text{H}_2\text{O}$	$\text{H}_2\text{HgCl}_4.7\text{H}_2\text{O}$	
			$\text{H}_2\text{HgCl}_4.7\text{H}_2\text{O}$		

The corresponding potassium salts, with the exception of the first, were first prepared by Bonsdorf (see Abegg's *Handbuch der anorg. Chem.*, II, 2).

It is here assumed that the compounds  $\text{NaHgCl}_3$ ,  $\text{NaHg}_2\text{Cl}_4$ , and  $\text{NaCl}$  in the same (water) solution dissociate to the same extent. The degree of dissociation of the corresponding divalent ions will then be equal to<sup>1</sup> ( $\gamma^2$ ), so that the dissociation factors in the equilibrium equations cancel out and we have

$$\frac{(\text{HgCl}_3)^-}{(\text{HgCl}_2)(\text{Cl})^-} = K_1. \quad (3) \qquad \frac{(\text{Hg}_2\text{Cl}_6)^-}{(\text{Hg}_2\text{Cl}_4)(\text{Cl})^-} = K_3. \quad (5)$$

$$\frac{(\text{HgCl}_4)^{--}}{(\text{HgCl}_3)(\text{Cl})^-} = K_2. \quad (4) \qquad \frac{(\text{Hg}_2\text{Cl}_6)^{--}}{(\text{Hg}_2\text{Cl}_5)(\text{Cl})^-} = K_4. \quad (6)$$

Expressing now these equations in terms of the known quantities  $(\text{HgCl}_2)$ ,  $(\text{Hg}_2\text{Cl}_4)$ ,  $\Sigma\text{HgCl}_2$ , and  $\Sigma\text{NaCl}$  and collecting common terms into  $N$ ,  $M$ ,  $N'$  and  $M'$  we finally obtain

$$-\frac{N}{2M} \pm \sqrt{\frac{\Sigma(\text{HgCl}_2) - (\text{HgCl}_2) - (2\text{Hg}_2\text{Cl}_4)}{M}} + \left(\frac{N}{2M}\right)^2 =$$

$$-\frac{N'}{2M'} \pm \sqrt{\frac{\Sigma(\text{NaCl})}{M'}} + \left(\frac{N'}{2M'}\right)^2. \quad (7)$$

The concentrations of the  $\text{HgCl}_2$  and  $2\text{Hg}_2\text{Cl}_4$  are obtained from partition measurements as described in a previous paper.<sup>2</sup> By means of Equation 7, in which the only unknown quantities are the equilibrium constants (included in  $N$ ,  $M$ ,  $N'$  and  $M'$ ), we can test the accuracy of the extrapolated constants, which were derived as follows:

From a study of the velocity of the reaction<sup>3</sup> between mercuric chloride and sodium formate to form  $\text{HgCl}_4^{2-}$  it was found that the specific reaction rate gradually decreased with increase in concentration of  $\text{NaCl}$  formed in the reaction, but that in very dilute solution, the velocity coefficients remained practically constant during the entire course of the reaction, because the amount of complex compounds formed under these conditions is extremely small. It may, therefore, be safely assumed, as a first approximation, that in the experiment with 0.03 molal mercuric chloride and 0.01 molal of sodium chloride, the chief sodium chloride complex in the solution is  $\text{NaHgCl}_3$ , as indicated in Equation *a*. Introducing the results of this experiment in Equation 3, it was found that

$$\frac{(\text{HgCl}_3)^-}{(\text{HgCl}_2)(\text{Cl})^-} = K_1 = 9.8 \text{ at } 25^\circ. \quad (8)$$

The amount of  $\text{HgS}$  obtained from the analysis of  $3/4$  of the benzene phase or 150 cc., was 0.0745 g., corresponding to 0.002141 mol of mercuric chloride per liter of solution of benzene phase, and this was denoted by  $\text{Cb}$ . If now  $R_\infty$  denotes the true distribution ratio (11.9) of mercuric chloride between water and benzene then,  $\text{Cb}R_\infty$  = the concentration of the

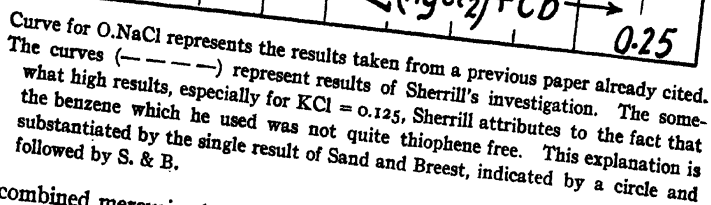
<sup>1</sup> Adams and Rosenstein, *THIS JOURNAL*, 36, 1464 (1914).

<sup>2</sup> *Loc. cit.*

<sup>3</sup> *THIS JOURNAL*, 37, 73 (1915).



**pe•lite**


$$\frac{(\text{Hg}_2\text{Cl}_4)}{(\text{HgCl}_2)^2} = K = 0.3.$$

Now substituting the experimental results in Equation 8 we have

$$\frac{\Sigma(\text{HgCl}_2) - (\text{Cb}) - (\text{CbR}_\infty) - 2K(\text{Cb})^2(\text{R}_\infty)^2}{(\text{CbR}_\infty)[\Sigma(\text{NaCl}) - (\text{NaHgCl}_2)]} = 9.8. \quad (9)$$

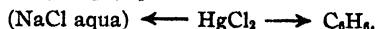
(In the paper just cited (10)<sup>4</sup>  $K = 3$ ,  $K$  being calculated on the basis of millimols instead of mols per liter of solution as in the above.)

In order to evaluate  $K_2$ ,  $K_3$  and  $K_4$ , the following experiments were performed:<sup>1</sup>

TABLE I.—25°.

Expt. No.	$\Sigma(\text{NaCl})$ .	$\Sigma(\text{HgCl}_2)$ + (Cb).	HgS from 150 cc. $\text{C}_6\text{H}_6$ (g.).	(Cb).	$\Sigma(\text{HgCl}_2)$ .	R.
Series I.						
(a).....	0.000	0.100	..	0.007400	0.092600	12.51
(b).....	(0.005)	(0.100)	..	(0.007210)	....	..
1.....	0.050	0.100	0.2003	0.005756	0.094244	13.01
2.....	0.125	0.100	0.1372	0.003943	0.096057	24.36
3.....	0.250	0.100	0.0748	0.002149	0.097851	45.52
4.....	0.500	0.100	0.0259	0.000744	0.099256	132.96
Series II.						
1.....	0.125	0.15	0.2223	0.006388	0.143612	22.48
2.....	0.250	0.15	0.1316	0.003781	0.146219	38.67
3.....	0.500	0.15	0.0468	0.001345	0.148655	110.52
Series III.						
1.....	0.125	0.20	0.3099	0.008905	0.191095	21.46
2.....	0.250	0.20	0.1974	0.005672	0.194328	34.26
3.....	0.500	0.20	0.0782	0.002247	0.197753	88.01
Series IV.						
1.....	0.250	0.25	0.2668	0.007667	0.242333	31.61
2.....	0.500	0.25	0.1167	0.003353	0.246647	73.55

<sup>1</sup> In order to determine the relative amounts of the several complex substances in the solution, the distribution ratios



were measured. This method was preferred because it is capable of yielding results of a very high degree of accuracy, if the method of analysis, given in a previous paper dealing with the distribution ratio of mercuric chloride between water and benzene, is strictly followed.

The reliability of this method of determining the mercuric chloride in the benzene phase is even more evident in this work than in the previous as a glance at the distribution ratios will show. Thus in Table I, Expt. 4, a 0.2% error in the water phase would correspond to a 21% error in the benzene phase, if the latter were determined by difference. It was therefore deemed desirable and sufficient to determine the amount of mercuric chloride in the benzene phase only, and to take the difference between the initial concentration and the amounts thus found as the quantity of mercuric chloride in the water phase. The experimental procedure was exactly the same in every detail as already described in a previous article (THIS JOURNAL, 37, 260 (1915)) except that the desired amount of pure sodium chloride was added to the contents of of the 250 cc. flask before it was filled to the mark with distilled water at the desired temperature.

In the above table  $\Sigma(\text{NaCl})$  denotes the total concentration of the sodium chloride in the water phase in mols per liter of solution.

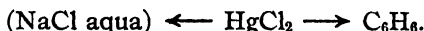
$\Sigma(\text{HgCl}_2) + (\text{Cb})$  denotes the total concentration of the mercuric chloride in the water phase and benzene phase.

$\text{HgS}$  from 150 cc.  $\text{C}_6\text{H}_6$  denotes the number of grams of mercuric sulfide obtained from the analysis of  $\frac{3}{4}$  of the benzene phase, the total being 200 cc.

$(\text{Cb})$  denotes the number of mols of mercuric chloride in the benzene phase in mols per liter of solution.

$\Sigma(\text{HgCl}_2)$  denotes the total number of mols, both free and combined, of mercuric chloride in the water phase per liter of solution.

$R$  denotes the distribution ratio of the system



Since, in Experiment 4, Series I, the amount of free mercuric chloride is very small, as is evident from the amount of mercuric chloride found in the benzene phase, then, according to Equations *a*, *c* and *e*, the only complex ions we need to consider here (as a first approximation) are  $(\text{HgCl}_3)^-$  and  $(\text{HgCl}_4)^{--}$ . Substituting the results of this experiment into Equation 9 we have:

$$\frac{(\text{HgCl}_3)^-}{(\text{HgCl}_2)(\text{Cl})^-} = \frac{\Sigma(\text{HgCl}_2) - (\text{Cb}) - (\text{CbR}_\infty) - 2K(\text{Cb})^2(R_\infty)^2 - (\text{Na}_2\text{HgCl}_4)}{(\text{CbR}_\infty)[\Sigma(\text{NaCl}) - (\text{NaHgCl}_3) - (2\text{Na}_2\text{HgCl}_4)]} = 9.8$$

Whence  $\text{Na}_2\text{HgCl}_4 = 0.06$ ,  $\text{NaHgCl}_3 = 0.03$ ,  $\text{NaCl} = 0.35$  and

$$\frac{(\text{HgCl}_4)^{--}}{(\text{HgCl}_3)^-(\text{Cl})^-} = 5.7 = K_2 \text{ approximately.}$$

Similarly an approximate value for  $K_3$  was obtained by plotting on a large scale  $\text{Cb}$  (millimols for 10 cm.) against  $\Sigma\text{NaCl}$  (millimols per 1 cm.) of Series I. The extrapolated values (given in Table I in parentheses) were then substituted into Equation 9,

$$\frac{(\text{HgCl}_3)^-}{(\text{HgCl}_2)(\text{Cl})^-} = \frac{\Sigma(\text{HgCl}_2) - (\text{Cb}) - (\text{CbR}_\infty) - 2K(\text{Cb})^2(R_\infty)^2 - (2\text{NaHg}_2\text{Cl}_5)}{(\text{CbR}_\infty)[\Sigma(\text{NaCl}) - (\text{NaHgCl}_3) - (\text{NaHg}_2\text{Cl}_5)]} = 9.8,$$

where, according to Equations *a* and *b* we may, as a first approximation, neglect the quantities  $\text{Na}_2\text{Hg}_2\text{Cl}_6$  and  $\text{Na}_2\text{HgCl}_4$ . We then obtain  $\text{NaHg}_2\text{Cl}_5 = 0.000188$ ,  $\text{NaHgCl}_3 = 0.002198$ ,  $\text{HgCl}_2 = 0.0858$ ,  $\text{NaCl} = 0.002614$  and  $\text{Hg}_3\text{Cl}_4 = 0.002209$ , and finally

$$\frac{(\text{Hg}_3\text{Cl}_4)^-}{(\text{Hg}_3\text{Cl}_4)(\text{Cl})^-} = 33 = K_3 \text{ approximately.}$$

Finally  $K_4$  was obtained by substituting the approximate values for the equilibrium constants and the experimental results of every experiment

into the general Equation 7. The four equilibrium constants thus obtained were then readjusted in order to satisfy the summation Equations 1 and 2.<sup>1</sup> The final results are given in Table II, the headings being self-explanatory.

TABLE II.

	(HgCl <sub>2</sub> ).	$\frac{(\text{HgCl}_2)^-}{\gamma}$	$\frac{(\text{HgCl}_2)^{--}}{\gamma^2}$	(Hg <sub>2</sub> Cl <sub>2</sub> ).	$\frac{(\text{Hg}_2\text{Cl}_2)^-}{\gamma}$	$\frac{(\text{Hg}_2\text{Cl}_2)^{--}}{\gamma^2}$	$\frac{(\text{Cl})^-}{\gamma}$
Series I.							
1.....	0.068496	0.017050	0.002120	0.001407	0.001250	0.000632	0.026196
2.....	0.046915	0.030280	0.010098	0.000661	0.001621	0.002100	0.068703
3.....	0.025578	0.036841	0.026626	0.000196	0.001086	0.003121	0.152579
4.....	0.008856	0.031000	0.054200	0.000024	0.000328	0.002248	0.355776
Series II.							
1.....	0.076017	0.039687	0.010326	0.001733	0.003475	0.003583	0.054020
2.....	0.044995	0.051802	0.030104	0.000607	0.002721	0.006331	0.122607
3.....	0.016066	0.048600	0.071917	0.000077	0.000872	0.005087	0.296520
Series III.							
1.....	0.105970	0.046098	0.010137	0.003369	0.005800	0.005276	0.042276
2.....	0.067497	0.063800	0.031003	0.001367	0.005047	0.009600	0.099947
3.....	0.026741	0.066270	0.080912	0.000214	0.002019	0.009682	0.250523
Series IV.							
1.....	0.091238	0.076166	0.030049	0.002497	0.007733	0.012210	0.081583
2.....	0.039906	0.083257	0.084648	0.000478	0.003703	0.015237	0.213270
No. of expt.		$\frac{(\text{HgCl}_2)^-}{(\text{HgCl}_2)(\text{Cl})^-}$	$\frac{(\text{HgCl}_2)^{--}}{(\text{HgCl}_2)(\text{Cl})^-}$		$\frac{(\text{Hg}_2\text{Cl}_2)^-}{(\text{Hg}_2\text{Cl}_2)(\text{Cl})^-}$	$\frac{(\text{Hg}_2\text{Cl}_2)^{--}}{(\text{Hg}_2\text{Cl}_2)(\text{Cl})^-}$	
Series I.							
1.....	9.5		4.7		34		19
2.....	9.4		4.8		36		19
3.....	9.4		4.7		36		19
4.....	9.8		4.9		38		19
Series II.							
1.....	9.7		4.8		37		20
2.....	9.4		4.8		37		19
3.....	10.2		5.0		38		20
Series III.							
1.....	10.3		5.2		40		21
2.....	9.5		4.9		37		19
3.....	9.9		4.8		38		19
Series IV.							
1.....	10.2		4.8		38		19
2.....	9.7		4.8		36		19

Av.  $K_1 = 9.8$  Av.  $K_2 = 4.9$  Av.  $K_3 = 37$  Av.  $K_4 = 19$

<sup>1</sup> It does not seem justifiable to substitute the average values of the equilibrium constants thus obtained for  $K_1 = 9.8$ ,  $K_2 = 4.9$ ,  $K_3 = 37$ ,  $K_4 = 19$  in the general Equation 7 in order to obtain "calculated values" for Cb and compare them with the "Cb found," because the deviations of the equilibrium constants from the corresponding average, although small, may well be due to the assumptions made in reference to their degree of association, which is only approximately correct.

## Conclusion.

(1) The complex compounds of mercuric chloride and sodium chloride which have been assumed to exist in water solution and whose presence have been confirmed sufficiently by experimental evidence, have all been prepared in solid crystalline form.

(2) No complex mercuric chloride of sodium, potassium or hydrogen has been shown to exist either in the solution or in solid form having a higher chloride content than is indicated by the type  $\text{Na}_2\text{HgCl}_4$ . It is especially interesting to note that from a saturated solution of mercuric chloride and hydrochloric acid at about  $-10^\circ$  no compound richer in HCl than  $\text{H}_2\text{HgCl}_4$  could be obtained by Ditte, although the solution was supersaturated with HCl gas. This is a conclusive test since the increase of the hydrochloric acid content in these compounds with the fall in temperature should be favorable, due to the fact that the solubility of hydrochloric acid increases with a decrease in temperature while the solubility of mercuric chloride decreases.

(3) The complex  $\text{H}_3\text{HgCl}_5$  given in Abegg's *Anorganische Chemie*<sup>1</sup> by Ley is the result of a misunderstanding of the original data from which it was calculated, as is shown below.

16°.		
Mols HCl. a.	Mols $\text{HgCl}_2$ . c.	a/c.
1.57	1.52	1.0
2.09	2.83	1.0
4.03	4.34	1.0
6.44	5.11	1.3
9.51	5.06	1.7
16.00	6.37	2.0
22.00	6.90	3.3

From these figures Ley concluded that a compound containing the anion  $(\text{HgCl}_2)_x(\text{Cl})_{2x}$  must exist in solution. As a matter of fact on consulting the original data, it was found that Ditte claims to have added the

## SOLUBILITY RESULTS OF DITTE.

16°.				
Ditte's original data.		Calculated from original data.		
Grams HCl to 100 grams $\text{Hg}_2\text{O}$ . a.	Grams $\text{HgCl}_2$ to 100 grams of solution a. b.	$\frac{(b-6.8)}{271}$ d.	$\frac{100a}{(a+100)36.5}$ c.	c/d.
0.0	6.8	0.000	0.000	—
5.6	46.8	0.148	0.145	1.0
10.1	73.7	0.247	0.252	1.0
13.8	87.8	0.299	0.332	1.1
21.6	127.4	0.447	0.488	1.1
31.0	141.9	0.499	0.649	1.3
50.0	148.0	0.521	0.912	1.8
68.0 sat.	154.0	0.548	1.110 sat.	2.0

<sup>1</sup> II, 2, p. 642.

mercuric chloride to 100 g. of the hydrochloric acid solutions, as is shown in the table above, and not to the amounts of hydrochloric acid contained in 100 g. of pure water as interpreted by Ley.

BERKELEY, CALIFORNIA.

[CONTRIBUTION FROM THE LABORATORY OF QUALITATIVE ANALYSIS, COLLEGE OF THE CITY OF NEW YORK.]

## A STUDY OF THE SILVER ARSENATE TEST FOR ARSENIC.

By L. J. CURTMAN AND P. DASCHAVSKY.

Received February 18, 1916.

The precipitation of arsenic in the form of an arsenate, by silver nitrate in a neutral solution is so striking that it recommends itself as an excellent confirmatory test. However, the results obtained by students in this laboratory have been so irregular that it was thought worth while to investigate this test for the purpose of ascertaining the conditions under which it could be relied upon to give constant results. It was also the object of the experiments recorded in this paper to determine whether this test is sufficiently sensitive to serve as a confirmatory test for amounts of arsenic from 1-5 mg.

**Preparation of Standard Sodium Arsenate Solution.**—41.6 g.  $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$  were dissolved in water and the volume made up to a liter. 20 cc. portions of this solution were run out from a buret and the arsenic determined gravimetrically by the method given by Treadwell.<sup>1</sup> The results of well-agreeing determinations gave the solution a value of 10 mg. of As per cc. By suitable dilution in volumetric flasks, solutions of lower concentrations were obtained.

**Determination of the Sensitiveness of the Test.**—By means of graduated pipets, definite amounts of the standard arsenate solution were introduced into a series of test tubes. 2 cc. of a silver nitrate solution of strength 50 mg. Ag per cc. were then added. After the addition of one drop of a 1% solution of phenolphthalein, the solutions were made alkaline with dilute  $\text{NH}_4\text{OH}$  and finally made just acid with 5% acetic acid. After standing for several minutes the tubes were examined and the results compared with a blank run under the same conditions. The following results were obtained:

TABLE I.

No.	As (mg.).	Result.	No.	As (mg.).	Result.
1	10.00	Heavy precipitate	5	0.10	Faint precipitate
2	5.00	Heavy precipitate	6-7	0.05	Faint precipitate on standing
3	1.00	Small precipitate	8-10	0.02	Brown coloration. Limit
4	0.50	Small precipitate	11-12	0.01	Negative

The above results show that the limit of the test (0.02 mg. in a volume of 3 cc.) represents a concentration of 1 part in 150,000. While this limit-

<sup>1</sup> Treadwell "Quantitative Analysis," translated by H. T. Hall (1904), p. 163.

ing amount of arsenic can be readily recognized when compared with a blank, decided and unmistakable results are obtained with 0.05 mg. which for routine qualitative work is the practical limit of the test. By the use of an indicator and a 5% solution of acetic acid, added drop by drop, a practically neutral solution is readily obtained.

**Influence of Ammonium Salts.**—In the above experiments care was taken to avoid the addition of an excess of  $\text{NH}_4\text{OH}$ . In systematic analysis the arsenate is formed by the solution of the sulfide in an excess of nitric acid and the test applied after the free acid has been neutralized by ammonia. This procedure results in the formation of ammonium salts which, it was thought, might diminish the sensitiveness of the test and thus account for the failure of students to detect from 1 to 5 mg. of arsenic. To ascertain whether or not ammonium nitrate exercises any influence on the test, the following experiments were made. The procedure was the same as that already described. The results are given in Table II.

TABLE II.

No.	As (mg.).	$\text{NH}_4\text{NO}_3$ , g.	Total Vol., cc.	Test.
1-6.....	1.0	0.0-5.0	8.0	Good
7-12.....	0.2	0.0-5.0	9.0	Good

The above results show that 5 g. of  $\text{NH}_4\text{NO}_3$  do not interfere with the detection of small amounts of arsenic by this test.

**Sensitiveness of the Test in Systematic Analysis.**—To determine whether small amounts of arsenic could be detected by this test in systematic analysis, the following test analyses were made. The procedure was as follows: The solution, the volume of which was about 20 cc., was neutralized with  $\text{NH}_4\text{OH}$ , 2.5 cc. conc.  $\text{HCl}$  added, heated to boiling and treated with  $\text{H}_2\text{S}$ . The volume was then made up to 100 cc. and again treated with  $\text{H}_2\text{S}$  till precipitation was complete. The precipitate was collected on a filter, transferred to a beaker, heated for 5 minutes with 10 cc. conc.  $\text{HCl}$ , diluted and filtered. The residue, after washing free from chlorides with hot water, was transferred together with the filter to an evaporating dish, boiled with 2 cc. conc.  $\text{HNO}_3$  till no more fumes of the oxides of nitrogen were given off, diluted and the mixture filtered on a small filter. The latter was then washed five times with water,

TEST ANALYSES.

No.	As (mg.).	Sb (mg.).	Sn (mg.).	Result.
1.....	5	...	...	Reddish ppt.
2.....	5	5	5	Reddish ppt.
3.....	5	500	...	Small reddish ppt.
4.....	5	...	500	Small reddish ppt.
5.....	5	250	250	Small reddish ppt.
6.....	1	250	...	Small reddish ppt.
7.....	0.5	250	...	Reddish cloudiness
8.....	0.0	250	...	Pale yellow coloration

the combined filtrate and washings concentrated to 2 cc. and transferred to a test tube. The test was then carried out in the manner already described in the determination of the sensitiveness of the test. The preceding results were obtained.

The preceding results show that the silver arsenate test is capable of detecting as little as 0.5 mg. of arsenic in systematic analysis.

### Summary.

1. With pure solutions of arsenate the test with silver nitrate is sensitive to 0.02 mg. of arsenic.

2. Ammonium nitrate, which is generally formed in carrying out this test, exercises no influence on the detection of 0.2 mg. of arsenic as sodium arsenate.

3. A procedure is given by which, in systematic analysis, the test is capable of detecting 0.5 mg. of arsenic with certainty.

NEW YORK, N. Y.

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## THE DETERMINATION OF ALUMINIUM AS OXIDE.

BY WILLIAM BLUM.<sup>1</sup>

Received May 10, 1916.

CONTENTS.—I. Introduction. II. General principles. III. Historical. IV. Precipitation of aluminium hydroxide. 1. Hydrogen electrode studies. (a) The method; (b) Results of experiments; (c) Conclusions from hydrogen electrode experiments. 2. Selection of an indicator for defining conditions of precipitation. 3. Factors affecting the form of the precipitate. 4. Precipitation in the presence of iron. V. Washing the precipitate. VI. Separation from other elements. VII. Ignition and weighing of the precipitate. 1. Hygroscopicity of aluminium oxide. 2. Temperature and time of ignition. 3. Effect of ammonium chloride upon the ignition. VIII. Procedure recommended. IX. Confirmatory experiments. X. Conclusions.

### I. Introduction.

Although a considerable number of precipitants have been proposed for the determination of aluminium, direct precipitation of aluminium hydroxide by means of ammonium hydroxide, followed by ignition to oxide, is most commonly used, especially if no separation from iron is desired, in which case special methods must be employed. While the general principles involved in this determination are extremely simple, it has long been recognized that certain precautions in the precipitation, washing, and ignition, are necessary if accurate results are to be obtained. While, however, most of these details have been studied and discussed by numerous authors, it is noteworthy that few publications or text books have taken account of all the factors. In the present paper it seems

<sup>1</sup> Published by permission of the Director of the Bureau of Standards. This paper will appear in somewhat more detailed form as Scientific Paper No. 286, copies of which can be obtained upon request addressed to the Bureau of Standards, Washington, D. C.



desirable, therefore, to assemble the various recommendations, and to consider their basis and their accuracy. No attempt has been made, however, to include a complete bibliography. The experiments described in this paper were conducted in 1912, in connection with a study of the determination of alumina in phosphate rock. As the latter research was interrupted, this paper is confined to the direct determination of aluminium as oxide.

## II. General Principles.

In precipitations of metallic hydroxides by means of ammonia or other bases, the process may be considered as a progressive hydrolysis, brought about by the neutralization of the acid continuously set free. In the case of such hydroxides as ferric hydroxide, which are practically insoluble in bases, it may be readily shown that the solubility is decreased and precipitation rendered more complete by the addition of an excess of the precipitant, thereby increasing the hydroxyl ion concentration. In the case of amphoteric hydroxides, however, such as aluminium hydroxide, it is obvious that an excess of the base is to be avoided, and it therefore becomes desirable to select that degree of alkalinity which will ensure most nearly complete precipitation, and at the same time avoid resolution of the precipitate. As will be shown later, the study of the progress of the precipitation, and the selection of the proper "end point" of precipitation can readily be accomplished by means of the hydrogen electrode, the conditions selected being subsequently defined by means of suitable indicators.

## III. Historical.

Early recognition of the fact that, when considerable excess of ammonia is used in the precipitation of aluminium hydroxide, appreciable amounts of aluminium pass into the filtrate, led to the time honored procedure of boiling out most of the free ammonia. The latter method, however, has its defects, owing to the attack of glass vessels by the hot ammoniacal solution (leading to contamination of the precipitate with lime, silica, etc.); and to the possible resolution of alumina, when through excessive boiling the solution becomes slightly acid. Various authors have therefore urged the use of a very slight excess of ammonia with only a short period of boiling,<sup>1</sup> especially when a considerable amount of ammonium chloride is present in the solution.<sup>2</sup> While the beneficial effect of ammonium chloride in reducing the solubility of aluminium hydroxide in ammonia, has been pointed out by numerous authors, and has formed a basis

<sup>1</sup> S. L. Penfield and D. N. Harper, *Am. J. Sci.*, **32**, 107 (1886); *Chem. News*, **54**, 90, 102 (1886); W. H. Dautt, *J. Ind.-Eng. Chem.*, **7**, 847 (1915).

<sup>2</sup> Malaguti and Durocher, *Ann. chim. phys.*, [3] **17**, 421 (1846); J. Hanamann, *Z. anal. Chem.*, **3**, 367 (1864); C. F. Cross, *Chem. News*, **39**, 161 (1879); L. Blum, *Z. anal. Chem.*, **27**, 19 (1888); G. Lunge, *Z. angew. Chem.*, **1889**, 634.

for the procedures recommended in most text books, few attempts have been made to explain this effect, which in some cases has been attributed to the coagulation of the colloidal aluminium hydroxide by the salt.<sup>1</sup> While undoubtedly this is an important function of the ammonium chloride, it will be shown later that the reduction of the alkalinity (hydroxyl ion concentration) of ammonia by the presence of ammonium chloride also exerts a marked influence upon the completeness of precipitation.

While many authors recommend the customary method of using an indicator such as litmus paper to detect roughly the presence of an excess of ammonia, few have suggested the accurate definition of the desired alkalinity by means of suitable indicators. Hinrichsen<sup>2</sup> used rosolic acid in a study of the effect of fluorine upon the precipitation of aluminium by ammonia, but gives no experimental or theoretical basis for its selection. Numerous authors, in efforts to develop methods for the volumetric determination of aluminium or for testing the neutrality of aluminium salts, have used various indicators for determining the beginning and completion of the precipitation of aluminium hydroxide; but few, if any, have shown that complete precipitation actually occurs at the color change selected.

#### IV. Precipitation of Aluminium Hydroxide.

##### *i. Hydrogen Electrode Studies.*

(a) **The Method.**—The application of the hydrogen electrode to a study of the changes taking place in solution during precipitations was suggested in a paper on the determination of magnesia in limestone,<sup>3</sup> and was elaborated in an article by J. H. Hildebrand,<sup>4</sup> in which are given numerous curves for such precipitations, including the action of sodium hydroxide upon aluminium sulfate. The principle of the method is very simple, involving the measurement of the electromotive force of a cell consisting of a hydrogen electrode and a calomel half cell, immersed in the solution to be investigated. The hydrogen ion concentration of the solution may then be calculated from the formula

$$\log \frac{1}{[H^+]} = \frac{\pi - 0.338}{0.058}$$

where  $\pi$  is the observed e. m. f. in volts (at 25°). The apparatus and method of measurement were essentially those used by Hildebrand and Harned, precautions being taken to exclude carbon dioxide during the titrations.

<sup>1</sup> A. Classen, "Quantitative Analysis," p. 145, 6th Ger. Ed. (1912).

<sup>2</sup> *Z. anorg. Chem.*, **58**, 88 (1908). Hinrichsen showed that fluorine may hinder or entirely prevent the precipitation of aluminium hydroxide by ammonia.

<sup>3</sup> J. H. Hildebrand and H. S. Harned, *Orig. Com. 8th Intern. Congr. Appl. Chem.*, **1**, 217 (1912).

<sup>4</sup> *THIS JOURNAL*, **35** 864 (1913).

(b) **Results of Experiments.**—The data obtained by measurement of the changes in hydrogen ion concentration occurring upon addition of alkaline hydroxides to solutions of aluminium chloride are shown graphically in Fig. 1. The abscissas represent cubic centimeters of

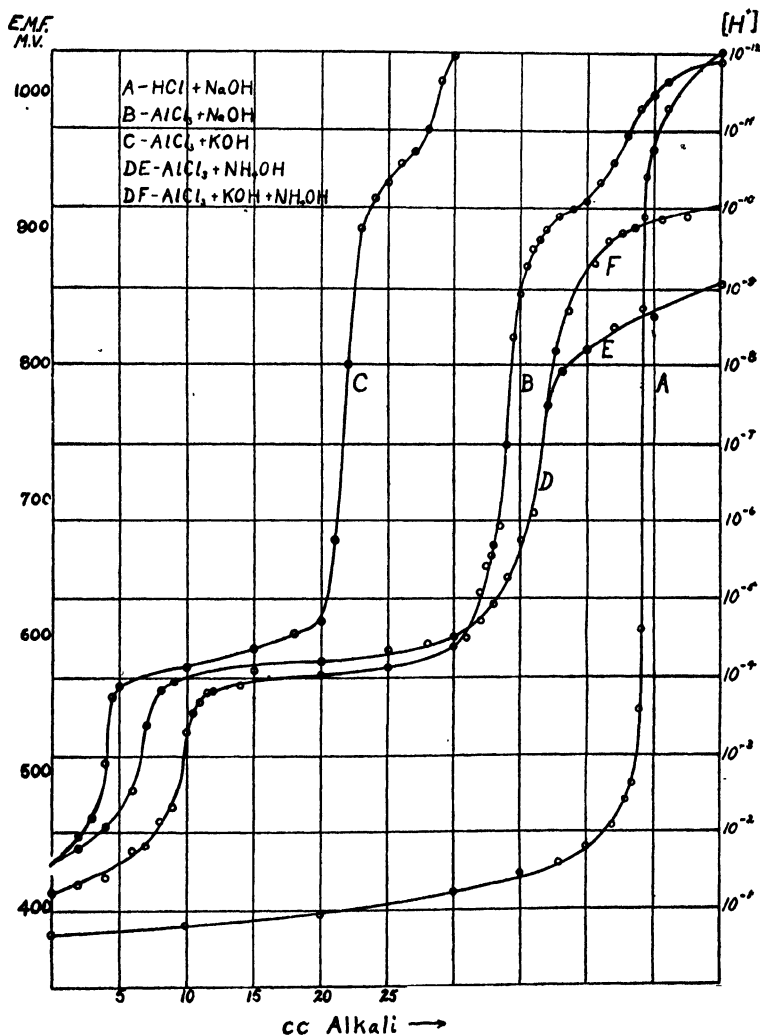


Fig. 1.—Precipitation of aluminium hydroxide.

alkaline hydroxide added, and the ordinates on the left side are the observed e. m. fs. expressed in millivolts. On the right side the value of the ordinates is expressed in terms of hydrogen ion concentration, calculated as previously stated. Curves A, B, and C, are the same as were

published in a preceding article by the author<sup>1</sup> on the constitution of aluminates. The curve A for the neutralization of hydrochloric acid with sodium hydroxide is shown simply to indicate the normal course of such a reaction in the absence of any metals precipitable as hydroxides. While Curves B and C are chiefly of interest in relation to the formation of aluminates, they are included here in order to show the similarity in the course of the precipitations with fixed alkalis and with ammonia.

The Curve DE shows the progress of the reaction when ammonium hydroxide is added to a solution of aluminium chloride containing a small amount of free acid. In order to eliminate the influence of ammonium chloride (to which reference will be made later) the Curve DF was plotted, in which the portion F was obtained by the addition of ammonium hydroxide to a solution, in which the aluminium hydroxide had been exactly precipitated by the addition of a calculated amount of potassium hydroxide. While the Curve F should strictly, therefore, be attached to Curve C, it has been placed in its present position in order to emphasize the comparison between the effect of ammonium hydroxide with and without the presence of ammonium chloride.

(c) **Conclusions from Hydrogen Electrode Experiments.**—From the curves shown in Fig. 1, it is evident that the changes taking place during the precipitation of aluminium chloride are practically independent of the alkali used. In general, it may be seen that precipitation<sup>2</sup> begins when  $[H^+]$  is about  $10^{-3}$  and is complete before  $[H^+]$  is  $10^{-7}$ . In the case of the fixed alkalis it was pointed out in a former paper that appreciable resolution of the precipitate, probably with the formation of aluminates, occurs soon after the neutral point is passed, *e. g.*, when  $[H^+]$  is less than  $10^{-9}$ . When ammonium hydroxide is used as the precipitant, it may be seen from the Curve DE, that it is difficult to obtain a solution in which  $[H^+]$  is less than  $10^{-9}$ , even when appreciable excess of ammonia is present. While, therefore, as is to be expected, it is not possible by this method to obtain complete solution in ammonia of any considerable quantity of aluminium hydroxide,<sup>3</sup> an appreciable amount was always

<sup>1</sup> W. Blum, *THIS JOURNAL*, 35, 1499 (1913).

<sup>2</sup> By "precipitation" in this sense is meant the chemical formation of  $Al(OH)_3$ , which (especially in the absence of salts) may not actually coagulate or form a visible precipitate, until from one-third to half of the alkali required for complete precipitation has been added. The point at which a visible precipitate occurred in the different experiments was found to be very variable. The formation of such regular curves as are shown, however, indicates the improbability of the existence in solution of any definite basic salts such as have been supposed to be formed by solution of freshly precipitated aluminium hydroxide in neutral aluminium chloride or sulfate solutions. Consult H. W. Fischer, *Habilitationsschrift*, Breslau, 1908, C. B., 1909, I, 260; R. Kremann and K. Hüttinger, *Jahrb. K. K. Geol., Reichsan.*, 58, 637 (1909); C. B., 1909, II, 1200.

<sup>3</sup> *Existence of Ammonium Aluminate.* In a previous communication the evidence

found dissolved in any solutions in which  $[H^+]$  is less than  $10^{-9}$ . The effect of even small amounts of ammonium chloride in reducing the alkalinity of ammonium hydroxide is clearly shown by comparison of Curves E and F, there being present no ammonium chloride in F, and in E only the amount  $[H^+]$

equivalent to about 37 cc. of 0.2 N  $NH_4OH$ , i. e., the solution at the end was about 0.08 N in  $NH_4Cl$ . This effect of ammonium chloride is also illustrated in Fig. 2, in which the hydrogen ion concentration of various ammonia-ammonium chloride solu-

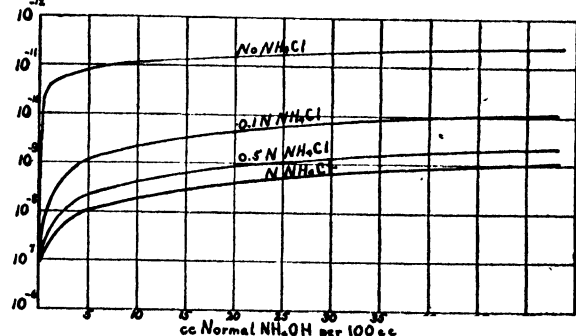


Fig. 2.—Effect of ammonium chloride upon the alkalinity of ammonia.

tions has been calculated from the ionization constant of ammonia at  $25^\circ$ .<sup>1</sup>

$$\frac{[NH_4^+][OH^-]}{[NH_4OH]} = 1.8 \times 10^{-5}$$

and that of water  $K_{w25^\circ} = 1.1 \times 10^{-14}$ , upon the assumption that the mass law holds for such solutions. For the sake of simplicity the ionization of ammonium chloride, which in solutions from N to 0.1 N varies from 75 to 85%,<sup>2</sup> has been taken as 80%. For convenience the results have been expressed in cc. of N ammonium hydroxide present in a volume of 100 cc. of ammonium chloride solutions of various concentration.

in favor of the formation in solution of definite aluminates of sodium and potassium was presented. While no such definite evidence of the existence of ammonium aluminate is available, owing to the above mentioned impossibility of securing ammonia solutions of high alkalinity, there seems to be no reason to doubt the analogy of the solutions in ammonia and the fixed alkalis. In this connection, it is interesting to consider the evidence presented by C. Renz (*Ber.*, 36, III, 2751 (1903)). This author dismisses the possibility of the existence of an ammonium aluminate, even though by an indirect method (*viz.*, solution of  $Al(OH)_3$  in  $Ba(OH)_2$  and subsequent addition of  $(NH_4)_2SO_4$ ) he was able to obtain a clear solution free from  $Ba^{++}$  and  $SO_4^{--}$ , 50 cc. of which contained 0.1 g.  $Al_2O_3$ . The fact, observed by Renz, that freshly precipitated  $Al(OH)_3$  is readily soluble in organic amines, far from being an argument against the existence in solution of ammonium aluminate, would appear to indicate that by the solution of aluminium hydroxide in any base, aluminates are formed, the maximum concentration being dependent upon the alkalinity of the resultant solution and its consequent ability to repress the hydrolysis of the aluminate.

<sup>1</sup> A. A. Noyes and R. B. Sosman, "Electrical Conductivity of Aqueous Solutions," *Carnegie Inst. Pub.*, 63, 228 (1908).

<sup>2</sup> F. W. G. Kohlrausch and L. Holborn, "Leitvermögen der Elektrolyte," p. 159 (1898).

From Fig. 2, it is evident (1) that even small additions of ammonium chloride cause a marked decrease in the alkalinity of ammonium hydroxide solutions, (2) that above 0.5 *N* an increase in the concentration of ammonium chloride has little effect, and (3) that with any reasonable concentration of ammonium chloride, it is impracticable to so limit the alkalinity that a solution in which  $[H^+]$  is less than  $10^{-9}$  (*i. e.*, one which dissolves appreciable  $Al(OH)_3$ ) is not formed when any large excess of concentrated ammonia is added. (It should be noted that 50 cc. *N*  $NH_4OH$  is about equal to 3.3 cc. conc.  $NH_4OH$ , sp. gr. 0.90.)

## 2. Selection of an Indicator for Defining the Conditions of Precipitation.

In Table I are shown the results of experiments conducted to determine which of the common indicators is most satisfactory for defining the completion of the precipitation. In each case the solution of the aluminium chloride and indicator was heated just to boiling in a platinum dish, and dilute ammonium hydroxide (about 2 *N*) was added till the first definite color change occurred. The solution was boiled for about two minutes, filtered and evaporated to dryness, and the total residue weighed after expulsion of the ammonium salts. Corrections were made for the small amounts of impurities in the distilled water and the ammonium chloride.

TABLE I.

Precipitation of  $Al(OH)_3$  by  $NH_4OH$ , Using Various Indicators.

(The  $AlCl_3$  solution, equivalent to 0.10 g.  $Al_2O_3$  was precipitated in a volume of 200 cc.)

Expt.	Indicator.	Color change $[H^+] =$ approx. <sup>1</sup>	$NH_4Cl$ added, g.	$Al_2O_3$ in filtrate.	Remarks.
1.....	<i>p</i> -Nitrophenol	$10^{-6}$	5	0.0010	
2.....	<i>p</i> -Nitrophenol	$10^{-6}$	5	0.0012	
3.....	Methyl red	$10^{-6.5}$	0	appreciable	Coagulated poorly
4.....	Methyl red	$10^{-6.5}$	5	0.0001	
5.....	Methyl red	$10^{-6.5}$	5	0.0000	
6.....	Rosolic acid	$10^{-7.6}$	0	0.0000	
7.....	Rosolic acid	$10^{-7.6}$	5	0.0000	
8.....	Rosolic acid	$10^{-7.6}$	5	0.0002	Macerated paper used
9.....	Phenolphthalein	$10^{-9}$	0	0.0004	
10.....	Phenolphthalein	$10^{-9}$	5	0.0004	

From Table I it is evident that considerable aluminium hydroxide remains unprecipitated when the solution is just alkaline to *p*-nitrophenol, while a smaller amount, but still appreciable, is redissolved when the solution is just alkaline to phenolphthalein. So far as accuracy is concerned, there is no choice between the use of methyl red and of rosolic acid. Practically, however, methyl red has been found preferable, because of its sharper color change, and because the end point is reached while approaching neutrality, *i. e.*, a slight excess of ammonia is less

<sup>1</sup> The approximate points of color change selected were measured with the hydrogen electrode at room temperature.

likely to cause resolution. Moreover, solutions just alkaline to methyl red are less likely to attack Jena or similar glassware, than are solutions slightly alkaline to rosolic acid. In using methyl red, however, it is essential to have appreciable ammonium chloride present to facilitate coagulation. The fact that coagulation occurs more readily, even in the presence of only small amounts of ammonium chloride, when the solution is just alkaline to rosolic acid, *i. e.*, when  $[H^+]$  is less than  $10^{-7}$ , would appear to indicate that the  $OH^-$  ion itself exerts a coagulating effect upon the colloid.

### 3. Factors Affecting the Form of the Precipitate.

It is difficult to obtain a precipitated colloid, such as aluminium hydroxide, in a form that is readily filtered and washed. In general, it has been recognized that while short boiling is desirable to effect coagulation, longer boiling renders the precipitate slimy and difficult to filter. As previously noted, the use of ammonium chloride is advantageous in producing the well-known salt effect in the coagulation of such a precipitate, as well as in reducing the actual solubility. These two factors were the only ones found to have a favorable influence upon the method of precipitation. The conclusion of W. E. Taylor,<sup>1</sup> that if the solution be heated to just  $66^\circ$  before the addition of ammonia, and subsequently boiled, the precipitate is "granular," could not be confirmed by R. Sudgen<sup>2</sup> nor by the author. The recommendation of A. Guyard<sup>3</sup> to add glycerol to the solution before precipitating with ammonia, was tried, and no improvement in the character of the precipitate was noted, while about 5 mg. of  $Al_2O_3$  was found in the filtrate. Similarly, the procedure of R. E. Divine,<sup>4</sup> *viz.*, precipitation in the presence of tannic acid, while it produced an appreciable improvement in the character of the precipitate, yielded a filtrate containing from 1 to 5 mg. of  $Al_2O_3$ , depending upon whether the solution was boiled for some time, or was filtered after a couple minutes' boiling.

While, therefore, it seems impossible to specify satisfactory conditions for the rapid filtration of considerable amounts of aluminium hydroxide, it is believed that for amounts of alumina up to 0.10 g.  $Al_2O_3$ , the following conditions will yield fairly satisfactory results; *viz.*: (1) the presence of at least 5 g. of ammonium chloride in a volume of 200 cc., (2) addition of dilute ammonia to the nearly boiling solution until it is just alkaline to methyl red (or rosolic acid), (3) boiling for not more than 2 minutes, and (4) filtration without waiting long for the precipitate to subside. (In some cases the precipitate was found to settle quite readily; while

<sup>1</sup> *Chem. News*, 103, 169 (1911).

<sup>2</sup> *Ibid.*, 104, 35 (1911).

<sup>3</sup> *Z. anal. Chem.*, 22, 426 (1883).

<sup>4</sup> *J. Soc. Chem. Ind.*, 24, 11 (1905).

in others it showed a tendency to rise to the surface, and would not settle, even on long standing.) The addition of macerated filter paper before precipitation has been found advantageous in aiding filtration (and also ignition), especially of large amounts of the precipitate.

#### 4. *Precipitation in the Presence of Iron.*

As previously noted, it is often necessary to precipitate ferric and aluminium hydroxides together. This can readily be accomplished by the procedure above recommended, since it was found that ferric hydroxide is completely precipitated by ammonia before the solution is alkaline to methyl red or to rosolic acid. In case sufficient iron is present to obscure the color of the indicator, it may be precipitated first by the careful addition of ammonia, and caused to settle by short boiling, after which the color of the indicator can readily be recognized in the supernatant liquid and more ammonia added if necessary, or any decided excess of ammonia may be neutralized with dilute acid, and the solution again boiled.

#### V. *Washing the Precipitate.*

Upon washing precipitates equivalent to 0.10 g.  $\text{Al}_2\text{O}_3$ , with only 75 cc. of hot water, from 0.5 to 2 mg. of  $\text{Al}_2\text{O}_3$  was found in the washings. The obvious remedy, *viz.*, washing with a solution of a volatile ammonium salt such as ammonium chloride or nitrate, has been suggested by numerous authors.<sup>1</sup> From the standpoint of the "salt" action there appears to be no preference between ammonium nitrate and chloride. The former has been used most frequently partly because of its slight advantage in assisting combustion of the filter paper, and partly because of the opinion, still prevalent, though frequently disproven, that the presence of ammonium chloride during ignition would cause loss of alumina by volatilization of the chloride.<sup>2</sup> As pointed out by W. F. Hillebrand,<sup>3</sup> when the original solution contains chlorides and it is desired to evaporate the filtrate and washings in platinum, and expel ammonium salts, it is impractical to use ammonium nitrate in the wash water, owing to attack of the platinum vessels. In the present research, therefore, a hot 2% solution of ammonium chloride was used. It was found that there was no appreciable difference in the amount of alumina dissolved by the neutral ammonium chloride solution, and that rendered slightly alkaline with ammonia, the residues obtained from 100 cc. of the washings in each case being less than 0.3 mg. The use of solutions of the pure salts, with no addition of ammo-

<sup>1</sup> W. H. Daudt, *J. Ind. Eng. Chem.*, 7, 847 (1915); Penfield and Harper, *Am. J. Sci.*, 32, 107 (1886); W. Trautmann, *Z. angew. Chem.*, 26 (Aufsatz), 702 (1913).

<sup>2</sup> It has been shown by Daudt (*Loc. cit.*) that 1% ammonium chloride solution may be used for washing precipitates containing ferric hydroxide with no loss of iron by volatilization.

<sup>3</sup> U. S. Geol. Survey, *Bull.* 422, 99 (1910).



nia, is therefore recommended, especially as solutions rendered alkaline are more likely to act upon the glass of the wash bottle and become contaminated.

### VI. Separation from Other Elements.

Owing to the relatively gelatinous condition of the precipitated aluminium hydroxide, the only practical method of eliminating elements such as the alkalis, which are likely to be present in considerable amount in the solution, is to dissolve and reprecipitate. That such a procedure is quite efficient, may be judged by the fact that from a solution containing 0.1000 g.  $\text{Al}_2\text{O}_3$ , and 10 g. of sodium chloride in a volume of 200 cc., the precipitate obtained after a single precipitation, and washing ten times with 2% ammonium chloride, weighed 0.1071 g., and contained much NaCl, while a similar precipitate which was washed only five times, dissolved in hydrochloric acid, reprecipitated and again washed five times, weighed 0.1008 g., and contained only a trace of NaCl.

It is well recognized<sup>1</sup> that the separation of aluminium from such elements as zinc, manganese, nickel, and cobalt by means of ammonia is unsatisfactory, since the alkalinity required for the resolution of their hydroxides is such as to cause appreciable solution of the aluminium hydroxide also. Moreover, it was found that even in solutions just alkaline to methyl red, oxidation and precipitation of manganese occurred so rapidly as to preclude a quantitative separation. For such separations, therefore, other procedures, *e. g.*, the basic acetate method, must be employed.

The precipitation conditions above recommended have been found especially favorable in the separation from those elements such as barium, calcium, and strontium, and to a less extent, magnesium, whose carbonates are likely to be formed by absorption of carbon dioxide, and carried down by the precipitated alumina. It has been found experimentally that in solutions containing barium and calcium, which are neutral, or even slightly alkaline to rosolic acid (*i. e.*,  $[\text{H}^+] = 10^{-7}$  to  $10^{-7.5}$ ) it is impossible to form a precipitate of the carbonates by exposure to the atmosphere.<sup>2</sup> Aluminium hydroxide precipitates obtained from solutions

<sup>1</sup> A. A. Noyes, W. C. Bray and E. B. Spear, *J. Am. Chem. Soc.*, 30, 482 and 532 (1908).

<sup>2</sup> This observation is approximately in accordance with the result obtained by calculating the alkalinity of barium chloride or calcium chloride solutions (*e. g.*, 0.1 N), saturated with respect to the neutral carbonates, in equilibrium with the normal atmosphere (see J. Johnston, *THIS JOURNAL*, 37, 2001-20 (1915)). Thus, the ionization of 0.1 N barium chloride solution may be assumed as 70%, *i. e.*,  $[\text{Ba}^{++}]$  is 0.07. Since at 16° the solubility product  $[\text{Ba}^{++}] [\text{CO}_3^{--}]$  is  $7 \times 10^{-9}$ ,  $[\text{CO}_3^{--}]$  is equal to  $10^{-7}$ . In any solutions at 16° in equilibrium with an atmosphere containing  $\text{CO}_2$  with a partial pressure P, 
$$\frac{[\text{OH}^-]^2}{[\text{CO}_3^{--}]} = \frac{3.4 \times 10^{-11}}{P}.$$
 While the ordinary atmosphere

containing 0.1000 g.  $\text{Al}_2\text{O}_3$  and calcium and barium chlorides equivalent to 0.2 g.  $\text{CaO}$  and  $\text{BaO}$  respectively (*i. e.*, twice the amount of  $\text{Al}_2\text{O}_3$ ), and washed five times with 2% ammonium chloride solution, weighed 0.0998 and 0.0999 g., and were found to be free from calcium and barium.

The beneficial effect of ammonium chloride in the separation of aluminium from magnesium has long been recognized. Formerly it was explained by the formation of a double salt, though more recently it has been attributed to the repression by the ammonium chloride, of the alkalinity of the ammonium hydroxide, to a point insufficient to precipitate the magnesium hydroxide.<sup>1</sup> The latter view is confirmed by the results of Hildebrand and Harned,<sup>2</sup> who found that  $\text{Mg}(\text{OH})_2$  is not precipitated until  $[\text{H}^+]$  is less than  $10^{-9}$ ; and by the curves shown in Fig. 2 of this paper, in which the above effect of ammonium chloride is clearly shown. That the procedure recommended is effective in the separation of aluminium and magnesium, is shown by experiments in which aluminium hydroxide (equivalent to 0.10 g.  $\text{Al}_2\text{O}_3$ ) precipitated in the presence of magnesium chloride equivalent to 0.2 g.  $\text{MgO}$ , contained less than 0.0010 g.  $\text{MgO}$ .

## VII. Ignition and Weighing of the Precipitate.

### 1. Hygroscopicity of Aluminium Oxide.

The fact that ignited  $\text{Al}_2\text{O}_3$  readily absorbs water has been recognized and pointed out by many authors.<sup>3</sup> This property has in fact been made the basis for the recommendation of the use of  $\text{Al}_2\text{O}_3$  as a dehydrating agent.<sup>4</sup> It should be noted, however, that for the latter use the  $\text{Al}_2\text{O}_3$  should not be strongly ignited. Many of the experiments that have been conducted to determine the hygroscopicity of such substances as  $\text{Al}_2\text{O}_3$  have little bearing upon analytical procedures, since no distinction was made between the amount of water absorbed, and the rate of absorption, especially during the first few minutes' exposure. Tests at this Bureau

contains about 3 parts of  $\text{CO}_2$  in 10,000 the air in a laboratory may often contain 5 parts, or more, in 10,000. In such a case  $P = 5 \times 10^{-4}$ , and therefore  $[\text{OH}^-]$  is  $0.84 \times 10^{-7}$ . If  $K_{w10} = 0.5 \times 10^{-14}$ , then  $[\text{H}^+]$  is about  $0.6 \times 10^{-7}$ , or  $10^{-7.2}$ , *i. e.*, the solution must be slightly alkaline before any  $\text{BaCO}_3$  can be precipitated by exposure to air containing the normal amount of  $\text{CO}_2$ .

From similar calculations for 0.1 *N*  $\text{CaCl}_2$ , assuming that  $[\text{Ca}^{++}][\text{CO}_3^{--}] = 0.98 \times 10^{-8}$ , it may be shown that  $[\text{OH}^-] = 1.0 \times 10^{-7}$ ; or  $[\text{H}^+] = 0.5 \times 10^{-7}$  or  $10^{-7.3}$  before any  $\text{CaCO}_3$  will be precipitated upon exposure to the atmosphere. (Since such carbonates are prone to form supersaturated solutions, precipitation may not occur even at the points designated.)

<sup>1</sup> J. M. Loven, *Z. anorg. Chem.*, **11**, 404 (1896); F. P. Treadwell, *Ibid.*, **37**, 326 (1903); W. Herz and G. Muhs, *Ibid.*, **38**, 138 (1904).

<sup>2</sup> *Orig. Com. 8th Intern. Congr. Appl. Chem.*, **1**, 217 (1912).

<sup>3</sup> E. T. Allen and V. H. Gottschalk, *Am. Chem. J.*, **24**, 292-304 (1900); Hess and Campbell, *THIS JOURNAL*, **21**, 776 (1899); C. F. Cross, *Chem. News*, **39**, 161 (1879).

<sup>4</sup> F. M. G. Johnson, *THIS JOURNAL*, **34**, 911 (1912).

have shown that in common with most substances capable of absorbing moisture (even those not intrinsically hygroscopic) recently ignited  $\text{Al}_2\text{O}_3$  absorbs within the first ten minutes' exposure to the atmosphere a large proportion of the water which it will absorb in twenty-four hours. Since, as frequently pointed out, the atmosphere in an ordinary desiccator which has recently been opened, is not greatly different from the atmosphere prevailing in the room, it is obvious that the all too common practice of placing in a desiccator ignited precipitates such as  $\text{Al}_2\text{O}_3$ , in uncovered crucibles, is likely to lead to even greater errors than are involved during the period required for rapid weighing. That a well fitting cover on a platinum crucible is efficient in preventing rapid absorption of moisture in the desiccator or on the balance, has been frequently demonstrated. Thus a crucible containing 0.10 g. ignited  $\text{Al}_2\text{O}_3$ , which when allowed to stand covered upon the balance, showed no appreciable change in weight in five minutes; gained as much as 0.0010 g. when uncovered for five minutes. For any accurate work in the determination of alumina, therefore, and especially in any experiments designed to test the temperature and period required for the ignition of such substances, it is absolutely essential that the crucible be well covered both in the desiccator and upon the balance.

## 2. Temperature and Time of Ignition.

Directions for the ignition of alumina<sup>1</sup> have usually prescribed blasting for periods varying from ten to thirty minutes, followed by successive short periods till constant weight is secured. While it is evident that in order to expel the last traces of moisture from such a precipitate, originally in a gelatinous condition, the use of a high temperature is desirable, it may be readily shown that long blasting is not necessary, at least for precipitates up to 0.2 g.  $\text{Al}_2\text{O}_3$ . In numerous experiments with 0.1 g.  $\text{Al}_2\text{O}_3$  the total loss in weight produced by various periods of blasting following the first five minutes' blasting, was less than 0.0002 g. In order to show conclusively that dehydration is complete after five or ten minutes' blasting (at a temperature from  $1100^\circ$  to  $1150^\circ$ ), a covered crucible (of especially pure platinum) containing 0.7 g.  $\text{Al}_2\text{O}_3$ , derived from three precipitates each of which had been blasted for five minutes, was again blasted for five minutes, and placed in a vacuum sulfuric acid desiccator, which was quickly exhausted. After cooling, the crucible was quickly weighed (against a tared crucible) and was then heated for three periods of ten minutes each to a temperature of  $1440^\circ$  to  $1460^\circ$  in an electric furnace.<sup>2</sup>

<sup>1</sup> H. Moissan, *Compt. rend.*, 121, 851 (1895); W. H. Daudt, *J. Ind. Eng. Chem.*, 7, 847 (1915); P. H. Walker and J. B. Wilson, *Chem. Eng.*, 16, 159 (1912), and numerous text books.

<sup>2</sup> Thanks are due to Messrs. R. B. Sosman and J. C. Hostetter of the Geophysical Laboratory for assisting in these high temperature experiments (in 1912).

The results of the experiment were as follows:

TABLE II.  
Ignition of  $\text{Al}_2\text{O}_3$ .

	Weight against tare. Grams.
Empty crucible.....	3.1665 g.
Including $\text{Al}_2\text{O}_3$ (previously blasted but exposed in transfer) ..	3.8953
After five minutes' blasting.....	3.8943
Weight of $\text{Al}_2\text{O}_3$ .....	0.7278
After 10 minutes at $1440-1460^\circ$ .....	3.8943
Additional 10 minutes at $1440-1460^\circ$ .....	3.8941
Additional 10 minutes at $1440-1460^\circ$ .....	3.8940
Weight of empty crucible after brushing out precipitate ...	3.1662
Weight of $\text{Al}_2\text{O}_3$ after heating.....	0.7278

From these results it is evident that, making allowance for the loss in weight of the platinum crucible (0.0003 g.), exposure to a temperature of over  $1400^\circ$ , produced no appreciable change in weight of  $\text{Al}_2\text{O}_3$  previously blasted for not over fifteen minutes.

From these results it is apparent that the continued losses in weight noted by some authors upon successive blastings of  $\text{Al}_2\text{O}_3$  were probably due, not to further dehydration of the precipitate, but to losses in weight of the crucibles (which in commercial platinum may be quite appreciable); or, in case the crucibles were not covered while in the desiccator and on the balance, to a decrease in the hygroscopicity of the precipitate. In other words, at no time was the true anhydrous weight obtained, but always a weight including some amount of absorbed moisture, which amount decreases (and may become almost negligible) after the precipitate has been heated to high temperatures for a considerable period. Owing to the frequent failure to mention whether the crucibles were covered during the ignition and weighing, it is impossible to determine in which cases the above criticism applies. Such omissions indicate, however, a lack of appreciation of the importance of covering the crucibles.

### 3. *Effect of Ammonium Chloride upon the Ignition.*

The still prevalent misconception that when aluminium hydroxide containing ammonium chloride is ignited, there is loss of aluminium, dates back at least to 1875.<sup>1</sup> It has been disproven so frequently<sup>2</sup> that it would be superfluous to dwell upon it were it not for the fact that it is still referred to in recent text books. The following experiments, while probably not essential to disprove this conception, are perhaps of interest in still further demonstrating the absence of such an effect. Measured portions of a pure  $\text{AlCl}_3$  solution were evaporated to small volumes in

<sup>1</sup> C. R. Fresenius, "Quantitative Analysis," 6 Ger. edition (1875).

<sup>2</sup> W. F. Hillebrand, U. S. Geol. Survey, *Bull.* 422, 99 (1910); Allen and Gottschalk, *Am. Chem. J.*, 24, 292-304 (1900); W. H. Daudt, *J. Ind. Eng. Chem.*, 7, 847 (1915).

weighed platinum crucibles, after which pure ammonia in slight excess was added. Evaporation was continued to dryness and the residues were heated till expulsion of all ammonium salts, and finally blasted and weighed. The results, together with those obtained by the method of precipitation, etc., recommended below (which had been found to give accurate results with metallic aluminium) are shown in Table III.

TABLE III.  
Effect of Ammonium Chloride upon Ignition.

Method.	Direct evaporation.		Precipitation.			
$\text{Al}_2\text{O}_3$ from 50 cc. $\text{AlCl}_3$ .....	0.0998	0.0997	0.1002	0.1001	0.1000	0.0999

From Table III it may be seen that in Expts. 1 and 2, where the aluminium hydroxide was certainly in very intimate contact with an excess of ammonium chloride, any loss of aluminium by volatilization was so small as to be negligible. Moreover, the weights in the last four experiments include corrections for the filter ash, and for known small impurities in the reagents and water, and therefore are probably somewhat less accurate than those obtained by direct evaporation.

### VIII. Procedure Recommended.

From the foregoing considerations the following conditions are recommended for the determination of aluminium hydroxide: To the solution containing at least 5 g. of ammonium chloride per 200 cc. of solution (or an equivalent amount of hydrochloric acid) add a few drops of methyl red (0.2% alcoholic solution) and heat just to boiling. Carefully add dilute ammonium hydroxide dropwise until the color of the solution changes to a distinct yellow. Boil the solution for one to two minutes, and filter at once. Wash the precipitate thoroughly with hot 2% ammonium chloride (or nitrate) solution. Ignite in a platinum crucible, and after the carbon is all burned off blast for five minutes, cover the crucible and place it in a desiccator till cool. Weigh (covered) as rapidly as possible. A second blasting of five minutes is desirable, especially as it permits a more rapid weighing, and consequently probably more accurate results.

### IX. Confirmatory Experiments.

A weakness of many of the published researches upon the determination of aluminium is the lack of suitable standards by which to test the proposed methods. The use for this purpose of hydrated salts of possibly uncertain hydration, such as the alums, is not to be recommended for accurate work, and in the few cases where metallic aluminium has been used, no detailed evidence of the purity has been presented. The following few experiments, though by no means exhaustive, show that the method just described will yield results accurate to at least one part in three hundred and probably better.

Two samples of the purest aluminium that could be obtained in 1912 from the Aluminum Company of American were analyzed by the methods described by J. O. Handy,<sup>1</sup> yielding the following results for the only elements that could be detected:

TABLE IV.  
Analysis of Aluminium.

Sample.	A.	B.
Silicon.....	0.13%	0.16%
Copper.....	0.01	0.01
Iron.....	0.25	0.17
Aluminium (diff.).....	99.61	99.66

Weighed portions (about 1.3 g.) of these samples were dissolved in hydrochloric acid and the solutions were oxidized with a small amount of nitric acid, and filtered to remove silicon. The filtrates were diluted to measured volumes and aliquots used for the determination of aluminium as above described, about 0.25 g. of  $\text{Al}_2\text{O}_3$  being weighed in each determination. The ammonia was redistilled and all reagents carefully tested and found free from appreciable contamination. The weights of precipitates were corrected for the filter ash, and for the amount of  $\text{Fe}_2\text{O}_3$  corresponding to the iron found by the previous analysis. The results are shown in Table V.<sup>2</sup>

TABLE V.  
Aluminium Determination in Metallic Aluminium.

Expt.	Sample.	Weight of Sample. Gram.	Found.		Al %.	
			$\text{Al}_2\text{O}_3$ Gram.	Al. Gram.	Found.	By diff.
1.....	A	0.12980	0.2445	0.12967	99.90	99.61
2.....	A	0.12980	0.2443	0.12956	99.82	...
3.....	B	0.12884	0.2428	0.12877	99.95	99.66

### X. Conclusions.

From the above experiments the following conclusions may be drawn, many of which simply confirm those of previous investigators:

(1) From observations made with a hydrogen electrode and with suitable indicators, it was found that the precipitation of aluminium

<sup>1</sup> THIS JOURNAL, 18, 768 (1896).

<sup>2</sup> In calculating the weight of aluminium present in the  $\text{Al}_2\text{O}_3$  the 1916 atomic weight of Al = 27.1, has been used. It is at least interesting, though probably not significant with so few experiments, to note that if the round atomic weight 27 be used for Al, the values for % Al found, become, respectively, 99.73 and 99.67 for A, and 99.78 for B, i. e., approaching the amount found by difference, well within the experiment limit. No probable source of error in the determinations in Table V is likely to account for the existing discrepancies, amounting to from 0.0006 to 0.0008 g.  $\text{Al}_2\text{O}_3$ . More experiments are required to throw light upon these discrepancies. The point is merely mentioned as of interest in connection with the statement of F. W. Clarke ("Recalculation of the Atomic Weights," p. 268, 3rd edition (1910)) that "the atomic weight of aluminium needs reinvestigation."

hydroxide by ammonium hydroxide is complete when  $[H^+] = 10^{-6.5}$  to  $10^{-7.5}$ , points approximately defined by the color change of methyl red and of rosolic acid.

(2) The presence of ammonium chloride during precipitation is advantageous in limiting the alkalinity, and in coagulating the precipitate.

(3) Solutions of ammonium nitrate and chloride are equally satisfactory for washing the precipitate.

(4) The conditions of precipitation recommended are favorable for the simultaneous precipitation of aluminium and ferric hydroxides; and for their separation from calcium, strontium, barium, and magnesium.

(5) Crucibles containing ignited alumina should be kept covered in the desiccator and on the balance.

(6) For precipitates of from 0.1 to 0.2 g.  $Al_2O_3$ , five or ten minutes' blasting is sufficient.

(7) The presence of ammonium chloride during ignition causes no appreciable loss of alumina.

WASHINGTON, D. C.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF VIRGINIA.]

## THE ESTIMATION OF VANADIC ACID, AFTER REDUCTION BY METALLIC SILVER.

By GRAHAM EDGAR.

Received March 23, 1916.

Among the many reactions of vanadic acid to be found in the literature, that with metallic silver seems to have been almost overlooked by the numerous investigators who have studied the element vanadium. The only reference which the writer has been able to find bearing at all on this subject is the statement in a paper by Campbell and Griffin<sup>1</sup> that "silver, lead, copper and other elements were tried (as reducing agents on mixed uranyl and vanadyl solutions) but \* \* \* offered no advantages for this purpose." It is true that Perkins<sup>2</sup> reduced vanadic acid to the tetroxide by the action of hydriodic acid and metallic silver, but he considered that the function of the silver was merely that of absorbing the iodine set free in the reaction, and the possibility of any direct action between the silver and vanadic acid seems not to have been thought of.

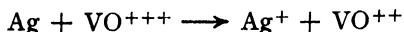
That silver should be capable of reducing pentavalent vanadium to tetravalent could be predicted with a considerable degree of certainty by consideration of the values obtained by Rutter<sup>3</sup> for the oxidizing potentials of solutions of vanadic acid, and also from the fact that silver is

<sup>1</sup> *J. Ind. Eng. Chem.*, **1**, 661 (1909).

<sup>2</sup> *Am. J. Sci.*, [4] **29**, 540.

<sup>3</sup> *Z. anorg. Chem.*, **52**, 368 (1907).

capable of reducing ferric salts, which are less easily reduced than solutions of vanadic acid. That the reduction cannot proceed further than the tetravalent stage (as it does in the case where zinc, magnesium or aluminum is used as the reducing agent) could also be predicted from the fact that divalent and trivalent vanadium salts precipitate metallic silver from solutions of silver salts.<sup>1</sup> We should expect therefore that the reaction



should be strictly quantitative—an expectation which is fully confirmed by the results given in this paper.

The course of the reaction can obviously be measured in three ways: (a) from the loss in weight of the metallic silver (if a weighed excess is used to effect the reduction); (b) by estimation of the dissolved silver (for example by titration with standard  $\text{NH}_4\text{CNS}$  solution); and (c) by oxidimetric estimation of the reduced vanadium, say, with standard  $\text{KMnO}_4$ . Provided the reaction is strictly quantitative, any one or all of these methods might be used for the quantitative estimation of vanadium.

To test the validity of these conclusions a series of experiments was carried out to determine the conditions, if any, under which a quantitative reduction of pentavalent vanadium to tetravalent might be expected.

#### Reagents and Apparatus.

Solutions of pure sodium vanadate (free from chloride) were carefully standardized against  $\text{KMnO}_4$ , after reduction with sulfur dioxide, and also by the very accurate method of Holverscheid.<sup>2</sup>

Potassium permanganate, approximately 0.05 *N*, was standardized against sodium oxalate.

Ammonium thiocyanate, approximately 0.05 *N*, was standardized against 0.1 *N* silver nitrate.

Metallic silver was prepared by electrolysis of a silver nitrate solution, using a platinum anode enclosed in a porous cup, and a fine platinum wire suspended near the top of the solution, as cathode. Under these conditions if a moderately heavy current is passed through the solution the silver is deposited as a "bush" of very fine crystals which drop continually from the cathode to the bottom of the beaker, and which can be later removed by filtration. The finely divided crystals were boiled with dilute sulfuric acid in order to remove any impurities which might be soluble in this medium, and were then filtered off through an alundum crucible, washed, and ignited at low red heat. In certain of the preliminary experiments other forms of silver were used, for instance, that formed by precipitation by zinc dust from dilute silver nitrate solution, or by

<sup>1</sup> Rutter, *Loc. cit.*

<sup>2</sup> *Inaug. Diss.*, Berlin, 1890.



igniting silver oxide, or in one case a spiral of pure fine silver wire. Mention is made of this in later discussion.

All pipets and burets used had been calibrated carefully and carried certificates of accuracy, and the greatest care was taken in making all measurements and readings. In all titrations the amount of the reagent necessary to produce the color change of the end point was determined by "blank" experiments and the readings were corrected accordingly. The amount was usually between 0.03 and 0.05 cc.

### Experimental Results.

After certain preliminary experiments which will not be recorded here, a number of determinations were made as follows:

Carefully measured portions of a standard solution of sodium vanadate were acidified with about 2 cc. of conc.  $\text{H}_2\text{SO}_4$ , diluted to about 75 cc., and treated with 1 to 2 g. of metallic silver, the exact weight of which had been previously determined. The small flasks containing the solutions were then placed upon a quartz plate, and the solutions were boiled gently for twenty minutes, or in some cases for one-half hour. Usually the boiling was continued for about ten minutes after the appearance of the pure blue color which signifies practically complete reduction of the vanadium. The solutions were then filtered upon asbestos in weighed perforated porcelain crucibles, and the residue of silver was washed with hot water. The crucibles were then placed inside of a larger nickel crucible and heated therein for about one-half hour, the outer crucible being subjected to the full heat of a large Bunsen burner. Under these conditions the inner porcelain crucible is at very low red heat. After cooling in a desiccator the crucibles were weighed, and the loss of weight of the silver was calculated.

The filtrates from the silver, containing all of the vanadium in the tetravalent condition, together with the dissolved silver, were titrated hot with 0.05  $N$   $\text{KMnO}_4$ . At the completion of this titration the solutions were cooled and titrated for silver with 0.05  $N$   $\text{NH}_4\text{CNS}$ , after the addition of ferric alum as indicator.

TABLE I.

No.	$\text{V}_2\text{O}_5$ taken, g.	Loss Ag, g.	$\text{KMnO}_4$ $N/20$ $\times 1.4212$ , cc.	$\text{NH}_4\text{CNS}$ $N/20$ $\times 0.9862$ , cc.	$\text{V}_2\text{O}_5$ calc. from Ag.	$\text{V}_2\text{O}_5$ calc. from $\text{KMnO}_4$ .	$\text{V}_2\text{O}_5$ calc. from $\text{NH}_4\text{CNS}$ .	Mean error, g.
1	0.0702	0.0830	10.85	15.65	0.0701	0.0702	0.0702	$\pm 0.0000$
2	0.0702	0.0832	10.85	15.68	0.0702	0.0702	0.0703	$\pm 0.0000$
3	0.0702	0.0828	10.87	15.60	0.0700	0.0700	0.0700	$-0.0001$
4	0.1260	0.1492	19.50	28.10	0.1260	0.1261	0.1260	$\pm 0.0000$
5	0.1260	0.1497	19.50	28.15	0.1264	0.1261	0.1262	$+0.0002$
6	0.1260	0.1490	19.50	28.20	0.1259	0.1261	0.1264	$+0.0001$
7 <sup>1</sup>	0.1260	0.1490	19.50	28.10	0.1259	0.1261	0.1260	$-0.0000$

<sup>1</sup> Reduced with silver wire; see below.

The amount of vanadic acid present was calculated (a) from the loss in weight of the metallic silver, (b) from the permanganate titration, and (c) from the silver equivalent to the thiocyanate titration. The results given in Table I show that the reaction is strictly quantitative, and that not only the gravimetric method, but also the volumetric ones are very accurate measures of the amount of vanadic acid present.

The value of these results is obvious. They afford an accurate and simple *gravimetric* method for the estimation of vanadium, which can in the same operation be checked by *two volumetric* estimations with very little additional trouble. Furthermore, if the gravimetric estimation is not desired, the operation can be very materially shortened and still permit the employment of the two volumetric estimations. In Table II are given the results of experiments in which the acid vanadate solutions were heated as above with unweighed amounts of metallic silver, filtered through paper or asbestos, and the filtrates titrated first with permanganate and then with thiocyanate as in the first set of experiments.

TABLE II.

No.	V <sub>2</sub> O <sub>5</sub> taken, g.	KMnO <sub>4</sub> N/20 × 1.4212, cc.	V <sub>2</sub> O <sub>5</sub> found calc. from KMnO <sub>4</sub> , g.	NH <sub>4</sub> CNS N/20 × 0.9862, cc.	V <sub>2</sub> O <sub>5</sub> found calc. from NH <sub>4</sub> CNS.	Mean error, g.
1	0.0702	10.85	0.0702	15.65	0.0702	±0.0000
2	0.0702	10.90	0.0704	15.70	0.0704	+0.0002
3	0.0702	10.85	0.0702	15.68	0.0703	+0.00005
4	0.1260	19.48	0.1259	28.10	0.1260	-0.00005
5	0.1260	19.50	0.1261	28.15	0.1262	+0.00015
6	0.1260	19.50	0.1261	28.10	0.1260	+0.00005

These results show that vanadic acid can be very accurately determined by titration with permanganate or thiocyanate, or both, after reduction by metallic silver.

**Discussion of Factors Influencing the Completion of the Reaction** (based partially upon the above experiments and partially upon the preliminary experiments, not here recorded).

**Time.**—The time necessary for complete reduction varied, naturally, with the total amount of vanadium present, with the amount of silver used, and with its state of subdivision. With as much as 2 g. of finely divided crystalline silver complete reduction of about 0.1200 g. of vanadic acid occurred after ten minutes' boiling. On the other hand, when only 0.5 g. of silver was used, reduction in some cases was incomplete after as much as one-half hour's boiling. The influence of the state of subdivision of the silver was shown by an experiment in which about 1.5 g. of fine silver wire was used as the reducing agent. In this case the gravimetric and volumetric estimation (Table I, No. 7) showed that reduction was complete, but this was only after an hour's boiling. The best prac-

tice seemed to be to continue boiling gently for about ten minutes after the solution had become a pure blue in color. Longer boiling, though unnecessary, is not harmful. Certain of the preliminary experiments showed that heating on the water bath for about two hours could usually be substituted for the boiling, but the results were not quite so certain.

**Preparation of Silver.**—No appreciable difference could be observed in the action of electrolytic silver, silver reduced by zinc, and silver prepared by heating the oxide, provided the purity was the same, and provided that preliminary treatment with dilute sulfuric acid was given. The electrolytic silver is, however, recommended as being more apt to be pure, and as giving somewhat more uniform results. It is easily prepared by the method given above.

**Acidity.**—The acidity of the solutions was varied between 0.5 cc. and 3 cc. of conc.  $\text{H}_2\text{SO}_4$  in a total volume of 75 cc. No very marked differences in behavior were observed, but somewhat more uniform results were obtained when 1 to 2 cc. in 75 cc. were used.

The reduction takes place readily when hydrochloric acid is used instead of sulfuric. In this case the dissolved silver is precipitated as chloride, and the vanadic acid present may be calculated from the *increase* in weight of the silver used for the reduction, as well as by permanganate titration of the filtrate. The gravimetric method is not quite so accurate as when loss of weight is determined, for, of course, the increase of weight due to chlorine is only about one-third of the decrease in weight caused by the solution of an equivalent amount of silver. Furthermore, the permanganate titration in the hot solution containing hydrochloric acid is not so accurate as in the presence of sulfuric acid alone, even when all precautions are observed. If it is desired, however, to determine vanadium in a solution containing hydrochloric acid, the silver reduction followed by permanganate titration may be used with a fair degree of accuracy. A better method is to remove the hydrochloric acid with silver sulfate in slight excess, and then determine vanadium as described above for solutions containing sulfuric acid. Either the gravimetric method or the permanganate titration may be employed, and even the thiocyanate titration also, provided a blank is run to determine the silver already present.

Nitric acid must not be present, for obvious reasons, nor any other substance acted upon by finely divided silver under the conditions of the experiment. The application of the reaction to the determination of vanadium in technical products, and in the presence of other substances, will be the subject of further investigation.

**Filtration.**—Where the gravimetric method is to be carried out, filtra-

tion through asbestos in a perforated porcelain crucible (or through alundum) is far preferable to filtration through paper. Where only the volumetric processes are to be carried out, filtration through paper is probably more convenient. It is even possible to wash the silver residue by decantation entirely, but filtration in this particular case is so rapid that decantation gains no time, and there is always the risk that fine particles of silver may be carried into the solution to be titrated, and thus spoil the determination.

**Accuracy.**—The accuracy with which duplication of results can be obtained is very unusual. This is especially true of the permanganate titration, where the writer had had as many as six consecutive titrations show no readable difference in the volume of permanganate used. Slightly greater variations were obtained in the thiocyanate titration, but here also the results are excellent. The writer has had experience with nearly all of the standard methods for the estimation of vanadium, and has obtained better results with the method proposed here than with any other of his experience. The fact that three check determinations may be made on the same solution should make the method admirably adapted to the exact standardization of vanadic acid solutions, or to other cases where high accuracy is desired.

Another useful feature of the method is the opportunity which it offers for the gravimetric standardization of permanganate solutions against metallic silver, or of comparing permanganate and thiocyanate solutions against one another. For this purpose complete reduction of the vanadic acid is not necessary, as the three factors, loss of weight of silver, permanganate titration, and thiocyanate titration are always strictly proportional, regardless of the extent to which the vanadium is reduced.

### Summary.

Vanadium is quantitatively reduced from the pentavalent to the tetravalent condition by metallic silver in acid solution under proper conditions.

The reaction may be used to determine vanadium (a) gravimetrically, from the loss in weight of the silver; (b) oxidimetrically, by titration with standard potassium permanganate; or (c) by titration of the dissolved silver with ammonium thiocyanate. All of these operations may be carried out on the same solution, and serve to check each other.

The results are of the highest order of accuracy.

The reactions may be also used for the standardization of permanganate solutions against silver, and of permanganate and thiocyanate solutions against each other.

## CONSTITUTION OF CHROMIC ACID.

[PART I.]

BY ASWINI KUMAR DATTA AND NILRATAN DHAR.

Received March 21, 1916.

From observations on the depression of the freezing point of aqueous solutions of chromium trioxide and the colorimetric study of the watery solutions of chromic acid, chromates and dichromates, and from the results of electrical conductivity measurements, Ostwald concludes that chromic acid solutions contain the strong acid  $\text{H}_2\text{Cr}_2\text{O}_7$  which forms neutral salts not appreciably hydrolyzed in aqueous solution. Costa,<sup>1</sup> from ebullioscopic measurements of chromic acid in aqueous solutions, shows that solutions not too concentrated contain the acid  $\text{H}_2\text{Cr}_2\text{O}_7$ . Spitalsky<sup>2</sup> arrived at similar conclusions from a study of the concentration of  $\text{H}^+$  in solutions of free chromic acid. Sabatier<sup>3</sup> tried to establish the identity of the spectra of chromic acid and dichromates, but no definite conclusion can be drawn from this work.

Sherril,<sup>4</sup> from an elaborate and careful study, considers that dilute solutions of  $\text{K}_2\text{Cr}_2\text{O}_7$  contain almost exclusively the ions  $2\text{K}^+$  and  $\text{Cr}_2\text{O}_7^{--}$  but that strong solutions of  $\text{K}_2\text{Cr}_2\text{O}_7$  are slightly acid owing to slight hydrolysis. Evidently Sherril has tried to amalgamate the two opposing views.<sup>5</sup>

Dubrisay<sup>6</sup> has shown that chromic acid differs from a strong dibasic acid, such as sulfuric acid, in exhibiting a constant surface tension only until the first acid function is neutralized, after which the surface tension decreases gradually but slightly until the second is neutralized.

Walden,<sup>7</sup> from conductivity measurements, adduces strong reasons in favor of the formula  $\text{H}_2\text{CrO}_4$ . Abegg and Cox<sup>8</sup> took the same view as that taken by Walden and they also add further reasons in support of this formula.

The present investigation is an attempt to assist in the solution of the problem by a study of further physical properties of chromium trioxide ( $\text{CrO}_3$ ) and  $\text{R}_2\text{Cr}_2\text{O}_7$  in solution.

## Molecular Volume in Solution.

If  $m$  is the molecular weight of a dissolved substance in grams,  $l$  the quantity of solvent which is present for every mol of solute,  $d$  the density

<sup>1</sup> *Gaz.* 36 (1906).

<sup>2</sup> *Z. anorg. Chem.*, 54, 265 (1907).

<sup>3</sup> *Compt. rend.*, 103, 49.

<sup>4</sup> *THIS JOURNAL*, 29, 1614 (1907).

<sup>5</sup> See also Dehn, *THIS JOURNAL*, 36, 829 (1914) for a colorimetric investigation of the chromates.

<sup>6</sup> *Compt. rend.*, 156, 1902 (1913).

<sup>7</sup> *Z. physik. Chem.*, 2, 70 (1888).

<sup>8</sup> *Ibid.*, 48, 725 (1904).

of the solvent and  $d$ , the density of the solution, the "Molecular solution volume",  $V_m$  is related to these as follows:

$$sV_m = \frac{m + l}{d_s} - \frac{l}{d}$$

From the molecular solution volume of a large number of substances, Traube calculated the atomic volume of the elements and the volume effects of a few of the chief modifications of structure and he also deduced from his extensive work a process for ascertaining the molecular weight of a substance in dilute aqueous solution. For dissolved substances we have the relation

$${}_sV_m = \Sigma nC + \phi_s,$$

where  $V_m$  is the molecular solution volume of the substance and  $\phi_s$  the molecular solution co-volume, which is approximately constant. In calculating  $\Sigma nC$  the atomic and structural constants for the substance in solution are used and, further, if the substance is an electrolyte, allowance is made for dissociation. This method has been successfully used in ascertaining the association factor of many substances.

The two possible formulas for chromic acid are  $\text{H}_2\text{CrO}_4$  and  $\text{H}_2\text{Cr}_2\text{O}_7$ . Now, all the above substances are strong electrolytes, chromic acid being a strong acid as has been determined from conductivity measurements and its chemical behavior.  $\text{H}_2\text{CrO}_4$  and  $\text{K}_2\text{CrO}_4$  are evidently of similar structure and so are  $\text{K}_2\text{Cr}_2\text{O}_7$  and  $\text{H}_2\text{Cr}_2\text{O}_7$ , and the difference between the molecular solution volume of  $\text{K}_2\text{CrO}_4$  and chromic acid, on the supposition that its formula is  $\text{H}_2\text{CrO}_4$ , should be equal to the difference between the solution volume of 2 atoms of potassium and 2 atoms of hydrogen. This also would be the difference between the molecular solution volume of  $\text{K}_2\text{Cr}_2\text{O}_7$  and chromic acid if its formula be  $\text{H}_2\text{Cr}_2\text{O}_7$ . It was found that the relation stated above holds good only when we take the formula for chromic acid as  $\text{H}_2\text{Cr}_2\text{O}_7$ .

TABLE I.  
Chromic Acid.

Density.	Acid per cc. as $\text{H}_2\text{CrO}_4$ (g.).	$v_m$ .	Acid as $\text{H}_2\text{Cr}_2\text{O}_7$ (g.).	$s_v m$ .
1.01480	0.02420	45.1	0.02250	73.6
1.00749	0.01210	44.6	0.01135	72.4
1.00503	0.00806	44.1	0.00750	72.0
1.00385	0.00605	43.0	0.00562	69.5
1.00256	0.00403	42.8	0.00375	69.0
		<hr/>		
		Mean, 44.0		70.9

The materials used were prepared in several ways and carefully purified by repeated crystallization and were dissolved in "Conductivity water" and kept in "Resistance glass" bottles. The strength of chromic acid was ascertained by adding excess of pure KI and titrating the iodine by

standard sodium thiosulfate. The density was determined by means of a Sprengel pyknometer as modified by Ostwald, following the details as given by him. The densities recorded above are the means of three determinations, agreeing to the fifth decimal place.

TABLE II.

Potassium dichromate.			Potassium chromate.		
Density.	Salt per cc. (g.).	$sV_m$ .	Density.	Salt per cc. (g.).	$sV_m$ .
1.01859	0.027144	90.9	1.01184	0.01488	39.5
1.00932	0.013572	91.4	1.02340	0.02976	40.5
1.00465	0.006786	92.2	1.01449	0.01863	42.0
1.00990	0.028240	87.0	1.00728	0.00931	41.9
1.00497	0.14120	87.0			
Mean, 89.7			Mean, 41.0		

Traube found the atomic volume, in solution, of hydrogen = 3.1 and of sodium = 1.8. He does not seem to have calculated that for potassium. We calculated the atomic volume in solution of potassium from the following data taken from "Physikalisch-chemische Tabellen":<sup>1</sup>

TABLE III.

Sodium Chloride.			Potassium Chloride.		
Density.	Salt per cc. (g.).	$sV_m$ .	Density.	Salt per cc. (g.).	$sV_m$ .
1.0401	0.0585	17.5	1.0444	0.0746	28.9
1.0788	0.01170	17.8	1.0887	0.1492	27.8
1.1164	0.01755	17.7	1.1317	0.2238	27.4
Av., 17.6			Av., 28.0		

Now sodium chloride and potassium chloride are both salts of similar nature. Their "structural constants" and "allowance for ionization" may be taken to be equal. The difference between their molecular volumes in solution is evidently that between the atomic volume in solution (A) of one atom of potassium and one atom of sodium. The atomic volume in solution of potassium is therefore 28 ( $sV_m$  for KCl) — 17.6 ( $sV_m$  for NaCl) + 1.8 (A for Na) = 12.2. This atomic constant of potassium may also be deduced as follows:

Traube<sup>2</sup> found the atomic volume (A) in solution of chlorine to be 13.2. Therefore

$$28.0 = 13.2 + A \text{ (for K)} + x \quad (1)$$

$$17.6 = 13.2 + 1.8 \quad + x \quad (2)$$

$x$  is a constant dependent on the nature of the salt and is the same for both KCl and NaCl, they being salts of the same nature.

From (1) and (2) we get A (for K) = 12.2. The two results are identical, showing the validity of our assumptions. The atomic volume

<sup>1</sup> Landolt and Bornstein, p. 177.

<sup>2</sup> Loc. cit.

in solution of potassium can therefore be taken to be 12.2. The difference between the solution volume of 2 atoms of potassium and 2 atoms of hydrogen is therefore  $12.2 \times 2 - 3.1 \times 2 = 18.2$ . The molecular volume in solution of potassium dichromate as has been found is 89.7 and that of chromic acid on the supposition that its formula is  $\text{H}_2\text{Cr}_2\text{O}_7$  is 70.9. The difference is 18.8 in good agreement with the calculated number 18.2. The molecular volume in solution of potassium chromate is 41.0 and that of chromic acid on the supposition that its formula is  $\text{H}_2\text{CrO}_4$  is 44. The difference is  $-3$  instead of  $+18.2$ . We are thus lead to conclude that formula for chromic acid is  $\text{H}_2\text{Cr}_2\text{O}_7$  and not  $\text{H}_2\text{CrO}_4$ . The above line of reasoning seems to be clear and satisfactorily confirmed by experimental evidence. But we should mention here that it has been found that this method does not always yield the right result. Gioletti<sup>1</sup> has applied the method to some tautomeric compounds, and on the whole the results are not very encouraging. Acetoacetic ester has the molecular volume 126.9, while the calculated<sup>2</sup> volume for the enolic form is 127.9 and that for the ketonic structure is 132.8. Accordingly it might be supposed that the sample consisted entirely of the enolic tautomeride; but this is contrary to chemical experience and to the evidence from other physical sources.

### Refractivity.

Refractivity is both additive and constitutive.<sup>3</sup> The molecular refraction of a compound is the sum of the refraction equivalents of the elements which enter into the compounds, modified by the manner of combination. So by an examination of their refractive equivalent of a substance we may gain a knowledge about the molecular condition of the substance.

Molecular refractivity of a solid electrolyte is slightly altered by solution in water. The behavior of different salts is not uniform, some increase and others decrease in refractivity on passing into solution. The effect of dilution is pronounced with concentrated solution. It tends to be constant with dilution and in a moderately dilute solution it becomes fairly constant.

We determined the molecular refractivity of various solutions of chromates, dichromates and chromic acid by Pulfrich's refractometer, using a sodium flame as the source of light. A certain amount of the substance was dissolved in water and the refractive index and density of the solution were taken. From this the refractive equivalent,  $n - 1/d = m$  was calculated, where  $n$  is the refractive coefficient,  $d$  the density and  $m$

<sup>1</sup> *Gazz. chim. ital.*, 34, 208 (1904).

<sup>2</sup> Traube, *Ber.*, 29, 1715 (1896).

<sup>3</sup> Gladstone, *Proc. Roy. Soc.*, 439 (1868); 60, 140 (1896); Gladstone and Hilbert, *Trans. Chem. Soc.*, 67, 831 (1895).



the molecular weight of the compound. The refractive equivalent of the dissolved salt is obtained by deducting from the refractive equivalent of a solution of the form  $s + p\text{H}_2\text{O}$ , where  $s$  signifies one molecule of the salt—the value which corresponds with  $p \times \text{H}_2\text{O}$ . That is the refractive equivalent of the salt =  $\frac{u-1}{d}(m+x) - \frac{u'-1}{d'}x$ , where  $u$  is the refractive coefficient of the salt solution,  $d$  its density,  $m$  the molecular weight of the salt,  $x$  the weight of the solvent containing the gram molecular weight of the salt,  $u'$  the refractive coefficient of the solvent and  $d'$  its density.

TABLE IV.  
Chromic Acid.

Density.	$\mu$ of solution.	$\mu'$ of water.	Acid per cc. calculated as $\text{H}_2\text{CrO}_4$ .	Refractive equiv.	Acid per cc. cal. as $\text{H}_2\text{Cr}_2\text{O}_7$ .	Refractive equiv.
1.01480	1.336765	1.33174	0.02420	39.7	0.0225	73.4
1.00749	1.33431	1.33182	0.01210	39.1	0.01125	72.5
1.00507	1.33347	1.33174	0.00806	39.7	0.0075	73.4
1.00382	1.33313	1.33182	0.00605	39.9	0.00562	73.8
1.00256	1.33259	1.33182	0.00403	39.4	0.00375	72.8
				Av., 39.5		73.2

TABLE V.  
Potassium Chromate.

Density.	$\mu$ for solution.	$\mu'$ for water.	Salt per cc.	Refractive equivalent.
1.02340	1.33782	1.33182	0.02976	53.0
1.01184	1.33475	1.33182	0.01488	51.2
1.01449	1.33539	1.33182	0.018627	51.4
1.00728	1.33379	1.33182	0.009314	52.7
1.00361	1.33275	1.33182	0.0046567	52.9
				Av., 52.2

Potassium Dichromate.

Density.	$\mu$ of solution.	$\mu'$ of water.	Salt per cc. calculated as $\text{K}_2\text{Cr}_2\text{O}_7$ .	Refractive equivalent.
1.01859	1.336745	1.33197	0.027144	82.5
1.00932	1.33431	1.33193	0.013572	82.2
1.00465	1.33315	1.33195	0.006786	82.8
1.00303	1.33267	1.33193	0.004524	82.6
1.01909	1.33685	1.33197	0.028239	82.5
1.00990	1.33455	1.33197	0.014119	82.8
1.00497	1.33326	1.33197	0.00706	82.7

Av., 82.6

In the present case the solvent is water, its density is taken to be unity at the temperature of the experiments, which was about  $26^\circ$ . The density of the solutions is of course determined at the same temperature. The refractivity of water used in the solution was observed separately each time

the refractivity of the solution was observed. It was found that the refractivity of the water varied from day to day very slightly, the maximum deviation being 1' (one minute) in the reading of the scale of the instrument which affected the refractive coefficient only in the fifth decimal place. This slight variation was evidently due to slight change of temperature and partly to errors of experiments.

Gladstone and others have found the refractive equivalent of potassium atom = 8.1 and of hydrogen in acids = 3.5. The refractive equivalent of hydrogen in water and other nonionizable substances is 1.5, but the value for hydrogen in strong acids is 3.5.<sup>1</sup> The difference between the refractive equivalents of 2 atoms of potassium and two atoms of hydrogen is therefore  $16.2 - 7 = 9.2$ . By similar lines of reasoning as indicated in the case of molecular solution volume we can expect the difference between the refractive equivalents of potassium dichromate and chromic acid, on the supposition that its formula is  $H_2Cr_2O_7$ , to be 9.2. By actual experiments we find the difference to be  $82.6 - 73.2 = 9.4$ . If the formula of chromic acid be  $H_2CrO_4$  we should get the same difference between the refractive equivalents of potassium chromate and chromic acid ( $H_2CrO_4$ ). By experiment we find it  $52.2 - 39.5 = 12.7$  in place of 9.2. The formula of chromic acid is therefore  $H_2Cr_2O_7$  and not  $H_2CrO_4$ . This is also the conclusion arrived at from the study of volume relations.

Thus we see that two most important physical properties of chromic acid in solution are in support of the formula  $H_2Cr_2O_7$ , which also seems to be the more probable one from various other investigations.

In a subsequent paper, some other physical properties will be discussed.

PHYSICOCHEMICAL LABORATORY,  
PRESIDENCY COLLEGE, CALCUTTA.  
IMPERIAL COLLEGE OF SCIENCE,  
LONDON.

### NOTE.

**A Bottle for the Iodimetric Titration of Copper.**—Since L. W. Andrews<sup>2</sup> first described the use of iodate as a substitute for many iodimetric determinations, the method has been extended and is finding additional uses constantly. In technical practice particularly, the application to copper ores as described by Jamieson, Levy and Wells,<sup>3</sup> and by Brostrom<sup>4</sup> is finding much favor; in this method, there is formed hydrocyanic acid—a feature that militates against the use of the original shaking bottle as described by Andrews because of the pressure developed in shaking and the consequent forcible ejection of particles of liquid on removing the

<sup>1</sup> LeBlanc, *Z. physik. Chem.*, 4 (1889); Gladstone, *Phil. Mag.*, 15 (1870).

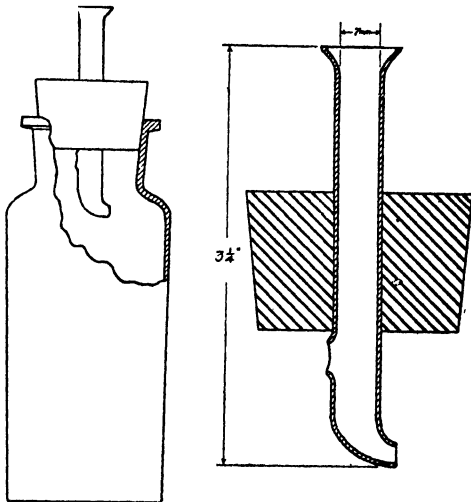
<sup>2</sup> THIS JOURNAL, 25, 756 (1903).

<sup>3</sup> *Ibid.*, 30, 760 (1908).

<sup>4</sup> *Eng. Mining J.*, 98, 215 (1914).

stopper between additions of iodate: on the other hand, the use of a simple open Erlenmeyer, as used in the Southwest copper district, limits more than desirable the freedom in shaking: both difficulties may be overcome by replacing the glass stopper by a two-hole rubber stopper, through which pass two glass tubes, 5-6 mm. in diameter and about 8 cm. long, one of the tubes being widened at the top to serve as an inlet for the iodate solution, the other serving as an outlet for vapor, their length preventing loss by ejection during shaking.

With a little additional trouble, a somewhat more efficient modification may be constructed: this is illustrated in the accompanying sketch. The tube is 7-8 mm. in diameter, flared above, narrowed and curved below, and provided with a blowhole just below the cork. This side hole acts not only as the pressure vent but also serves the purpose of washing the last drop of iodate down during the shaking without the use of a wash bottle.



This bottle has been in constant use by students for copper ore analyses in this laboratory for over a year and found quite satisfactory: besides its convenience, it saves the time required in removing the stopper or in shaking so very cautiously. The only objectionable feature is the action of chloroform or carbon tetrachloride on the rubber stopper if allowed to stand overnight: during titration the stopper is protected by an aqueous film and shows no deterioration even after long use.

O. DEXTER NEAL.

CHEMICAL LABORATORY, MISSOURI SCHOOL OF MINES,  
ROLLA, MO.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY,  
No. 265.]

## THE ADDITION COMPOUNDS OF PHENOLS WITH ORGANIC ACIDS.

BY JAMES KENDALL.

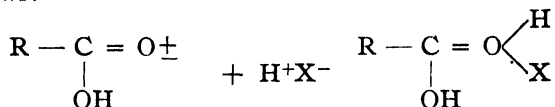
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It has been shown by the author in a recent communication<sup>1</sup> that *strong* organic acids (such as trichloroacetic acid) will combine directly with

<sup>1</sup> Kendall, *THIS JOURNAL*, 36, 1722 (1914).

weak organic acids (such as benzoic acid) to form equimolecular addition products. Compounds of this type are relatively unstable, in so far as they dissociate into their components to a considerable extent on fusion, but they can be readily isolated and identified by means of the freezing-point method described in a previous paper.<sup>1</sup> The stability of the addition products, as indicated by the curves obtained, increases with the difference between the acidic strengths of the two components.

The formation of compounds of this nature has been assumed to be due to the presence of the basic (or unsaturated) group  $\text{>C} = \text{O}^\pm$  in the weak acid. The oxygen atom in this group is potentially quadri-valent, and in the presence of a sufficiently strong acid the acidic properties of the weak organic acid are suppressed to such a degree that the basic nature of the group comes into prominence and an oxonium salt formation is obtained. The reaction is considered to be ionic and to take place as follows:



A great deal of evidence in favor of these views has been collected in a series of researches on organic substances of various types.<sup>2</sup>

The extension of this method of investigation to systems of the general type phenol-acid has seemed of importance to the author for several reasons. In the first place, most phenols belong to the class of weak organic acids and might therefore be expected to resemble them in exhibiting basic properties in the presence of a strong acid, with the consequent formation of oxonium salts analogous to those already described. Since, further, phenols in general are much more weakly acidic than the weak acids previously investigated (*e. g.*, benzoic acid); any addition products obtained should prove to be more stable in character, and less dissociated into their components in the liquid state.<sup>3</sup>

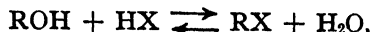
In the second place, the isolation and examination of addition compounds of the type phenol-acid are of interest because of the probability that the formation of such compounds constitutes an intermediate stage in the series of reactions involved in the direct production of phenolic esters of organic acids.<sup>4</sup> The general equation

<sup>1</sup> Kendall, *THIS JOURNAL*, **36**, 1222 (1914).

<sup>2</sup> Kendall and Carpenter, *Ibid.*, **36**, 2498 (1914); Kendall and Gibbons, *Ibid.*, **37**, 149 (1915).

<sup>3</sup> The validity of this assumption is discussed fully later (page 1320).

<sup>4</sup> Meuschutkin, *Ann.*, **197**, 220 (1879). The extent of the esterification, when equilibrium is reached, is only small (as in the case of the tertiary alcohols); hence the method is not available for the preparation of phenolic esters unless some dehydrating agent is added.



(where R is the aryl radical) merely shows the initial and end products, and gives no indication as to the mechanism of the reaction. The present investigation is thus immediately connected with the previous work of Kendall and Carpenter,<sup>1</sup> in which it was shown that phenols form with sulfuric acid stable addition compounds which may be regarded as intermediate products in the process of sulfonation.

In the complete examination of the field covered by systems of the general type phenol-acid, another point which deserves investigation is encountered. Phenols exhibit among themselves just as considerable a variation in acidic strength as do organic acids, consequently it is possible to construct systems which may be expected to behave quite differently from those already described. A convenient method of increasing the acidity of a phenol is to introduce nitro groups into the benzene nucleus. The effect of this will be to diminish the stability of the oxonium compounds obtained with strong acids, or even to prevent the formation of addition products altogether. By continued introduction of nitro groups into the nucleus we can obtain phenols (for example, picric acid) which are, indeed, quite as strongly acidic as the strongest organic acids. Such phenols may be expected to function similarly to *strong* acids, and to give oxonium compound formation both with *weak* acids and also with *weak* phenols. We can, therefore, by suitable variation of the acidic strengths of our two components, obtain most diverse examples of the general type, and these may be predicted to exhibit very different behavior when examined by the freezing-point curve method.

In the experiments tabulated below, this method has been employed in order to study the whole field, the acidic strengths of both phenols and acids being varied as widely as possible. As a typical strong acid, trichloroacetic acid has been chosen; it is easily obtained pure, has a convenient point of fusion, and has already been extensively used in previous work on addition compounds.<sup>2</sup> As a typical strong phenol, picric acid was selected; it is the simplest of its class and the most readily obtainable. Its disadvantages are a high melting point (which is unfavorable for the isolation of addition products, since their stability decreases with rise of temperature), the formation of dark-colored solutions with weak phenols (in which it is extremely difficult to detect the appearance or disappearance of crystals), and its highly explosive nature. The friction involved in the stirring of a molten mass largely consisting of picric acid constituted a source of constant danger, nevertheless it was found possible to complete the systems required with only a few minor accidents.

<sup>1</sup> Kendall and Carpenter, *Loc. cit.*

<sup>2</sup> Hence the results obtained here are directly comparable with those of previous papers. (See page 1317.)

The weak acids and phenols included in the investigation, with their ionization constants in aqueous solution at 25°, are given below.

Acids.	K.	Phenols.	K.
Acetic <sup>1</sup>	$1.85 \times 10^{-5}$	Phenol <sup>2</sup>	$1.15 \times 10^{-10}$
<i>o</i> -Toluic <sup>3</sup>	$12.0 \times 10^{-5}$	<i>o</i> -Cresol <sup>3</sup>	$0.63 \times 10^{-10}$
<i>m</i> -Toluic <sup>3</sup>	$5.14 \times 10^{-5}$	<i>m</i> -Cresol <sup>3</sup>	$0.98 \times 10^{-10}$
$\alpha$ -Toluic <sup>3</sup>	$5.56 \times 10^{-5}$	<i>p</i> -Cresol <sup>3</sup>	$0.67 \times 10^{-10}$
Chloroacetic <sup>3</sup>	$1.55 \times 10^{-3}$	Thymol <sup>2</sup>	$0.32 \times 10^{-10}$
Trichloroacetic <sup>3</sup>	$2.57 \times 10^{-1}$	<i>o</i> -Nitrophenol <sup>4</sup>	$6.8 \times 10^{-8}$
		<i>m</i> -Nitrophenol <sup>4</sup>	$1.0 \times 10^{-8}$
		<i>p</i> -Nitrophenol <sup>4</sup>	$6.5 \times 10^{-8}$
		$\alpha$ -Naphthol <sup>5</sup>	$1.0 \times 10^{-8}$
		$\beta$ -Naphthol	not determined
		Picric acid <sup>6</sup>	$2.52 \times 10^{-1}$

The ionization constants for the two strong acids employed, which are appended for comparison, are calculated for the concentration  $v = 32$ . The values given would, of course, change considerably with dilution, but the relative strengths of the two acids remain nearly constant. In alcohol, picric is the stronger acid<sup>7</sup> of the two.

The acids and phenols employed were either Kahlbaum specimens of a satisfactory degree of purity (as evidenced by the melting point) or were specially purified by recrystallization from a suitable solvent.

The experimental method followed was exactly as described in the previous papers of this series, the freezing-point curve of the two-component system being determined and all the desired information regarding the existence and stability of the addition products obtained being derived directly therefrom. In the tables below, T denotes the temperature of incipient solidification<sup>8</sup> of the mixtures, the compositions of which are expressed in molecular percentages. Examples of the curves obtained are reproduced in the accompanying diagram.

For convenience, the various types of systems examined from which oxonium salt formation may be expected are given under three divisions:

- I. Systems: weak phenol-strong acid (Tables 1-10).
- II. Systems: weak phenol-strong phenol (Tables 11-15).
- III. Systems: weak acid-strong phenol (Tables 16-19).

The fourth possible compound-forming type, systems: weak acid-strong acid, has already been fully investigated in a previous communication.<sup>9</sup>

<sup>1</sup> Kendall, *Medd. K. Vetenskapsakad. Nobelinst.*, Band. 2, No. 38 (1913).

<sup>2</sup> Ostwald, *Z. physik. Chem.*, 3, 418 (1889).

<sup>3</sup> Boyd, *J. Chem. Soc.*, 107, 1540 (1915).

<sup>4</sup> Holleman, *Rec. trav. chim. Pays-Bas*, 21, 432 (1902).

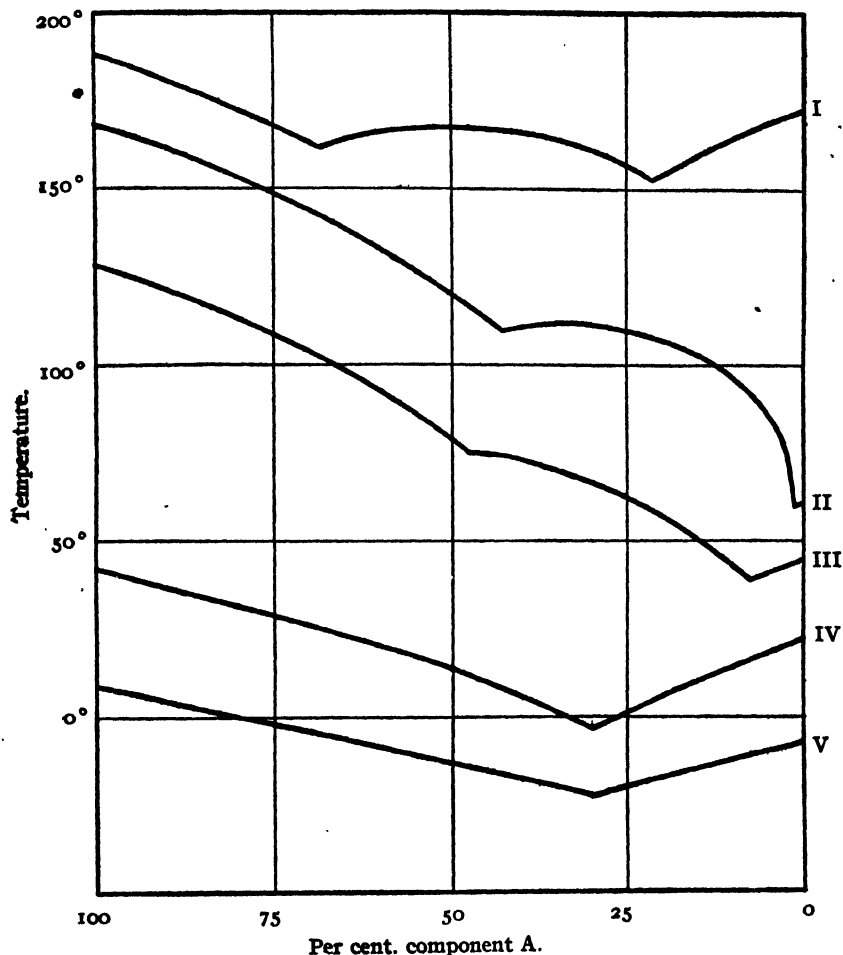
<sup>5</sup> Walden, *Ber.*, 24, 2025 (1891).

<sup>6</sup> Kendall, *Proc. Roy. Soc.*, (A) 85, 200 (1911).

<sup>7</sup> Snethlage, *Z. Elektrochem.*, 18, 543 (1912).

<sup>8</sup> All temperatures are corrected for exposed stem.

<sup>9</sup> Kendall, *THIS JOURNAL*, 36, 1722 (1914).



- I. Trichloroacetic acid-phenol. Subtract  $130^{\circ}$  from temperature scale.
- II. Picric acid-*m*-cresol. Subtract  $50^{\circ}$  from temperature scale.
- III. Picric acid-*p*-cresol. Subtract  $10^{\circ}$  from temperature scale.
- IV. Chloroacetic acid-phenol. Add  $20^{\circ}$  to temperature scale.
- V. Picric acid-*o*-toluic acid. Add  $110^{\circ}$  to temperature scale.

A system containing two components of not widely different acidic strength may be predicted not to give oxonium compounds. Thus, in the investigation quoted above, all examples of the two types: weak acid—weak acid and strong acid—strong acid gave on examination uniformly negative results. In the present work, a few examples of the types: weak phenol—weak acid and weak phenol—weak phenol are appended in order to cover the field completely and to illustrate that this rule holds for phenols also.

### I. Systems: Weak Phenol-Strong Acid.

Several investigations have been made on systems of this type by previous workers, but the results have been mainly negative, few addition compounds having been obtained. Maass and McIntosh<sup>1</sup> examined a great number of phenols with hydrobromic and hydrochloric acids, but isolated no compounds except in the case of resorcinol. Gomberg and Cone,<sup>2</sup> on the other hand, obtained addition products of orcinol, phloroglucinol and hydroquinone with HBr, but found no indication of compound formation with resorcinol and other phenols. Kendall and Carpenter<sup>3</sup> isolated a number of oxonium salts of phenols with sulfuric acid.

In the following table the positive results recorded in these researches are summarized: the compositions of the compounds obtained are indicated by condensed formula (A = phenol, B = acid) to economize space.

Systems.	Compounds.	Systems.	Compounds.
Resorcinol-HBr.....	AB <sub>4</sub>	Phenol-H <sub>2</sub> SO <sub>4</sub>	A <sub>2</sub> B
Resorcinol-HCl.....	AB <sub>3</sub> or AB <sub>4</sub>	<i>p</i> -Cresol-H <sub>2</sub> SO <sub>4</sub>	A <sub>2</sub> B; AB <sub>2</sub>
Orcinol-HBr.....	A <sub>2</sub> B	<i>o</i> -Xylenol-H <sub>2</sub> SO <sub>4</sub>	A <sub>2</sub> B; AB
Phloroglucinol-HBr.....	A <sub>2</sub> B	<i>p</i> -Xylenol-H <sub>2</sub> SO <sub>4</sub>	AB; AB <sub>2</sub>
Hydroquinone-HBr.....	?	<i>m</i> -Nitrophenol-H <sub>2</sub> SO <sub>4</sub>	A <sub>2</sub> B
		<i>p</i> -Nitrophenol-H <sub>2</sub> SO <sub>4</sub>	A <sub>2</sub> B

It will be noticed that no single case of compound formation has been previously recorded from a system of the simplest type—monobasic acid and monobasic phenol. The results obtained from such systems in the present investigation are given in the tables below.

1. **Phenol-Trichloroacetic Acid.**—The freezing-point curve of this system is shown in the diagram on page 1313. An equimolecular addition product, C<sub>6</sub>H<sub>5</sub>OH, CCl<sub>3</sub>.COOH, is indicated by the curve; this crystallizes out from a mixture of the two components in the form of beautiful white needles, m. p. 37.6°. The extraordinary flatness of the maximum for this compound on the freezing-point curve shows that it is very considerably dissociated into its constituents on fusion.

#### (a) Solid phase, CCl<sub>3</sub>.COOH.

% CCl <sub>3</sub> .COOH.....	100	90.2	82.6	75.7	68.8
T.....	57.3	50.7	45.2	38.9	31.9

#### (b) Solid phase, C<sub>6</sub>H<sub>5</sub>OH, CCl<sub>3</sub>.COOH.

% CCl <sub>3</sub> .COOH.....	65.1	63.1	60.0	57.0	53.7	50.2	44.8	41.1	35.4
T.....	34.0	34.9	36.0	36.8	37.4	37.6	37.2	36.3	34.2

#### (c) Solid phase, C<sub>6</sub>H<sub>5</sub>.OH.

% CCl <sub>3</sub> .COOH.....	18.3	13.2	7.2	0
T.....	25.9	31.8	37.0	42.4

<sup>1</sup> THIS JOURNAL, 33, 70 (1911).

<sup>2</sup> Ann., 376, 236 (1911).

<sup>3</sup> THIS JOURNAL, 36, 2498 (1914).



**2. *o*-Cresol-Trichloroacetic Acid.**—An exactly similar curve to that described above was obtained. The addition product,  $C_7H_7OH$ ,  $CCl_3$ .COOH, is stable at its maximum and highly dissociated on fusion; m. p.  $27.0^\circ$ .

(a) Solid phase,  $CCl_3$ .COOH.

% $CCl_3$ .COOH.....	100	90.3	82.7	76.0	64.6	56.0
T.....	57.3	50.3	44.4	38.3	25.6	15.3

(b) Solid phase,  $C_7H_7OH$ ,  $CCl_3$ .COOH.

% $CCl_3$ .COOH.....	60.5	56.0	50.8	45.5	40.1	35.0	30.2
T.....	25.3	26.6	27.0	26.7	25.3	23.4	20.8

(c) Solid phase,  $C_7H_7OH$ .

% $CCl_3$ .COOH.....	30.2	23.0	14.9	6.4	0
T.....	9.5	15.6	21.3	26.5	30.4

**3. *m*-Cresol-Trichloroacetic Acid.**—From this system the addition compound  $C_7H_7OH$ ,  $CCl_3$ .COOH was obtained, m. p.  $14.5^\circ$ . The curve resembles those of the preceding systems.

(a) Solid phase,  $CCl_3$ .COOH.

% $CCl_3$ .COOH.....	100	92.9	85.9	77.2	71.0	62.7	56.4
T.....	57.3	52.5	47.4	39.5	33.9	24.3	16.1

(b) Solid phase,  $C_7H_7OH$ ,  $CCl_3$ .COOH.

% $CCl_3$ .COOH.....	51.1	46.6	40.4	35.6	30.1	25.3
T.....	14.4	14.1	12.9	11.1	7.8	3.9

(c) Solid phase,  $C_7H_7OH$ .

% $CCl_3$ .COOH.....	15.5	8.8	0
T.....	—0.4	4.5	10.9

**4. *p*-Cresol-Trichloroacetic Acid.**—An equimolecular addition compound,  $C_7H_7OH$ ,  $CCl_3$ .COOH, was obtained, similar in its character to those already described; m. p.  $37.6^\circ$ .

(a) Solid phase,  $CCl_3$ .COOH.

% $CCl_3$ .COOH.....	100	91.6	85.1	76.9	70.0
T.....	57.4	51.6	46.9	39.9	32.3

(b) Solid phase,  $C_7H_7OH$ ,  $CCl_3$ .COOH.

% $CCl_3$ .COOH.....	63.5	58.3	53.1	49.2	44.8	37.0	29.9	22.2
T.....	34.7	36.4	37.4	37.6	47.0	34.5	30.2	23.5

(c) Solid phase,  $C_7H_7OH$ .

% $CCl_3$ .COOH.....	17.6	12.7	6.6	0
T.....	19.9	24.7	29.8	34.5

**5. Thymol-Trichloroacetic Acid.**—It was not found possible to isolate any compound from this system, probably owing to persistent supercooling.

(a) Solid phase,  $CCl_3$ .COOH.

% $CCl_3$ .COOH.....	100	92.2	84.6	76.4	69.1	62.0	55.2
T.....	57.3	52.8	46.8	39.6	32.1	23.5	15.0

(b) Solid phase,  $C_{10}H_{15}OH$ .

% $CCl_3$ .COOH.....	49.4	43.0	35.4	28.6	21.7	13.6	7.0	0
T.....	10.1	18.0	25.8	32.0	37.5	42.4	46.1	49.6

6. *o*-Nitrophenol-Trichloroacetic Acid.—No addition compound formation was indicated by this system.

(a) Solid phase,  $\text{CCl}_3\text{COOH}$ .

% $\text{CCl}_3\text{COOH}$ .....	100	92.0	84.8	77.7	68.9	59.8	51.0
T.....	57.3	52.8	47.8	41.9	34.1	26.2	18.1

(b) Solid phase,  $\text{C}_6\text{H}_4\text{NO}_2\text{OH}$ .

% $\text{CCl}_3\text{COOH}$ .....	48.6	40.5	33.3	25.1	21.1	11.9	6.0	0
T.....	17.6	23.1	27.9	32.4	34.6	39.6	42.1	44.7

7. *m*-Nitrophenol-Trichloroacetic Acid.—Here also no compound formation was obtained.

(a) Solid phase,  $\text{CCl}_3\text{COOH}$ .

% $\text{CCl}_3\text{COOH}$ .....	100	92.6	85.5	78.4	71.4
T.....	57.3	53.3	49.2	44.9	40.5

(b) Solid phase,  $\text{C}_6\text{H}_4\text{NO}_2\text{OH}$ .

% $\text{CCl}_3\text{COOH}$ .....	71.4	64.3	53.8	39.9	30.2	19.9	10.1	0
T.....	43.2	50.9	60.4	71.4	78.1	84.7	90.1	95.3

8. *p*-Nitrophenol-Trichloroacetic Acid.—The curve resembles that of the two preceding systems in indicating no compound formation.

(a) Solid phase,  $\text{CCl}_3\text{COOH}$ .

% $\text{CCl}_3\text{COOH}$ .....	100	94.1	87.7	81.8	75.8
T.....	57.3	54.4	51.2	47.8	44.0

(b) Solid phase,  $\text{C}_6\text{H}_4\text{NO}_2\text{OH}$ .

% $\text{CCl}_3\text{COOH}$ .....	70.6	59.4	45.5	30.3	16.0	0
T.....	51.0	65.1	79.7	92.6	103.7	113.8

9.  $\alpha$ -Naphthol-Trichloroacetic Acid.—No compound formation was indicated in this or the following system.

(a) Solid phase,  $\text{CCl}_3\text{COOH}$ .

% $\text{CCl}_3\text{COOH}$ .....	100	91.2	83.1	75.2
T.....	57.3	52.6	47.7	42.1

(b) Solid phase,  $\text{C}_{10}\text{H}_7\text{OH}$ .

% $\text{CCl}_3\text{COOH}$ ...	66.8	59.0	50.6	43.0	35.7	28.6	21.3	14.9	7.6	0
T.....	48.7	55.1	61.5	67.3	72.5	76.9	81.6	85.3	89.9	94.2

10.  $\beta$ -Naphthol-Trichloroacetic Acid.—

(a) Solid phase,  $\text{CCl}_3\text{COOH}$ .

% $\text{CCl}_3\text{COOH}$ .....	100	93.4	88.2	80.4
T.....	57.3	53.1	49.3	43.5

(b) Solid phase,  $\text{C}_{10}\text{H}_7\text{OH}$ .

% $\text{CCl}_3\text{COOH}$ .....	74.0	67.4	62.2	55.0	46.4	36.2	25.0	13.4	0
T.....	49.2	58.8	67.6	77.0	86.2	95.9	105.2	113.9	121.6

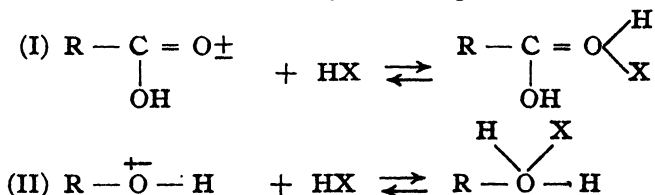
### Consideration of Results.

Of the ten phenols examined with trichloroacetic acid, four (phenol and the three cresols) gave equimolecular addition products. The flatness of the maxima on the freezing-point curves indicates that these compounds are very highly dissociated into their components on fusion. In the case of thymol no compound could be isolated, but the form of

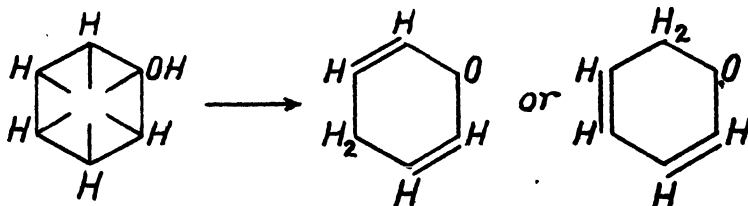
the curve leaves no doubt that combination with the acid has occurred.<sup>1</sup> The remaining five systems—the nitrophenols and the naphthols—show no trace of compound formation.

These results, when correlated with the table of acidic strengths on page 1312, are seen to fall in line with the assumptions made regarding the nature of the reaction in the introduction. The more weakly acidic phenols are just capable of forming oxonium salts with trichloroacetic acid and the slight increase in acidity in passing to the nitrophenols and the naphthols is sufficient to inhibit compound formation.

A disparity is evident, however, when the results are compared with those previously obtained for weak acids.<sup>2</sup> These, although of far greater acidic strength than the phenols, give more stable compounds with trichloroacetic acid. The explanation probably lies in the different nature of the group involved in the formation of the oxonium salt. In the case of acids, addition has been assumed to take place on the carbonyl oxygen,<sup>3</sup> whereas with the phenols the only oxygen present is in a hydroxyl group. Thus the two reactions may be distinguished as follows:



It is true that previous investigators<sup>4</sup> have assumed that phenols, in forming addition compounds, first pass over to a tautomeric ketonic form, *i. e.*,



<sup>1</sup> The depression of the freezing point of trichloroacetic acid by thymol is greater than that obtained with similar molecular proportions of the more highly acidic phenols. This slight "dip" (apparent in the curves for the acid in systems 1-5) indicates the presence of a compound in solution (Kendall, *THIS JOURNAL*, 36, 1731-3 (1914)).

<sup>2</sup> Kendall, *THIS JOURNAL*, 36, 1722 (1914).

<sup>3</sup> In conformity with previous workers (compare Hoogewerff and van Dorp, *Rec. trav. chim. Pays-Bas*, 21, 363 (1902)). Some addition, however, must also simultaneously occur upon the hydroxyl oxygen, with the formation of an oxonium

salt of the type:  $\text{R}-\overset{\text{O}}{\underset{\text{H}}{\text{C}}}=\overset{\text{X}}{\text{O}}-\text{H}.$

<sup>4</sup> Gomberg and Cone, *Ann.*, 376, 236 (1911).

(under which assumption addition takes place on the carbonyl group, as in the case of acids) but this is neither a necessary<sup>1</sup> nor, indeed, a satisfactory explanation of the compound formation. Alcohols and ethers, substances with which such a rearrangement is not possible, give well-defined oxonium salts with acids.<sup>2</sup> Here the carbonium structure suggested by Gomberg and Gone for the addition products is altogether excluded, since no double-bonded oxygen is present in the original molecule. The isolation by Maass and McIntosh<sup>3</sup> of addition compounds of resorcinol with acids also conflicts with the conclusions expressed by Gomberg and Cone.<sup>4</sup>

Our present data with regard to oxonium compounds of substances lacking the carbonyl group are, however, insufficient to enable any definite opinion to be expressed as to the mechanism of the reaction. If, as is probable, it forms the first stage in the formation of the phenolic esters or organic acids, then it would seem reasonable to infer that the reaction takes place in successive steps corresponding with those involved in the general process of esterification. The discussion of this subject will be taken up again in a subsequent communication.

## II. Systems: Weak Phenol-Strong Phenol.

The results of previous investigations upon systems of this type are summarized in the following table. It will be seen that a number of simple phenols have already been examined with picric acid, and in some cases addition compounds have been isolated:

Systems.	Compounds.	Observer.
Phenol-picric acid.....	AB	Philip <sup>5</sup>
<i>o</i> -Nitrophenol-picric acid.....	None	Kreemann and Rodinis <sup>6</sup>
<i>m</i> -Nitrophenol-picric acid.....	None	Kreemann and Rodinis
<i>p</i> -Nitrophenol-picric acid.....	None	Kreemann and Rodinis
$\beta$ -Naphthol-picric acid.....	AB	Kuriloff <sup>7</sup>
Catechol-picric acid.....	AB	Philip and Smith <sup>8</sup>
Guaiacol-picric acid.....	AB	Philip and Smith
Resorcinol-picric acid.....	AB	Philip and Smith

The methods employed in the above researches were substantially the same as those of the present paper, the existence and stability of the addition compounds being determined from the freezing-point curve. Consequently the results recorded above are directly available for comparison with those of this investigation, and only those phenols listed on

<sup>1</sup> Kendall and Carpenter, *THIS JOURNAL*, 36, 2511 (1914).

<sup>2</sup> Maass and McIntosh, *Ibid.*, 34, 1273 (1912).

<sup>3</sup> *Ibid.*, 33, 70 (1911).

<sup>4</sup> *Loc. cit.*, pages 236-7.

<sup>5</sup> *J. Chem. Soc.*, 83, 814 (1903).

<sup>6</sup> *Monatsh.*, 27, 152 (1906).

<sup>7</sup> *Z. physik. Chem.*, 23, 673 (1897).

<sup>8</sup> *J. Chem. Soc.*, 87, 1735 (1905).

page 1312 not hitherto examined with picric acid are therefore included here.

**11. *o*-Cresol-Picric Acid.**—An equimolecular addition compound,  $C_7H_7OH$ ,  $C_6H_2(NO_2)_3OH$ , was obtained, highly dissociated on fusion (as evidenced by the flatness of the maximum on the freezing-point curve), m. p.  $89.8^\circ$ . The compound crystallizes as beautiful yellow prisms from a very dark red solution.

(a) Solid phase,  $C_6H_2(NO_2)_3OH$ .

% $C_6H_2(NO_2)_3OH$ .....	100	89.1	80.9	72.7	65.5
T.....	118.5	110.5	104.1	96.5	89.1

(b) Solid phase,  $C_7H_7OH$ ,  $C_6H_2(NO_2)_3OH$ .

% $C_6H_2(NO_2)_3OH$ .....	62.0	57.7	49.7	42.0	34.1	27.5	19.9	13.5	9.2
T.....	87.4	89.0	89.8	89.1	86.7	83.3	76.9	68.9	60.8

(c) Solid phase,  $C_7H_7OH$ .

% $C_6H_2(NO_2)_3OH$ .....	1.6	0
T.....	29.4	30.4

**12. *m*-Cresol-Picric Acid.**—From this system the compound  $2C_7H_7OH$ ,  $C_6H_2(NO_2)_3OH$  was isolated, fine, yellow needles melting at  $61.6^\circ$ . The freezing-point curve is shown in the diagram on page 1313.

(a) Solid phase,  $C_6H_2(NO_2)_3OH$ .

% $C_6H_2(NO_2)_3OH$ .....	100	90.1	81.5	73.8	66.6	59.8	53.1	45.3
T.....	118.5	111.4	104.8	97.5	90.6	82.2	74.7	63.3

(b) Solid phase,  $2C_7H_7OH$ ,  $C_6H_2(NO_2)_3OH$ .

% $C_6H_2(NO_2)_3OH$ .....	41.7	37.4	32.4	28.6	23.6	19.6	14.6	9.9	5.7	3.4
T.....	60.0	61.2	61.5	60.8	58.7	56.5	52.6	46.7	38.5	30.3

(c) Solid phase,  $C_7H_7OH$ .

% $C_6H_2(NO_2)_3OH$ .....	1.1	0
T.....	10.2	10.9

**13. *p*-Cresol-Picric Acid.**—This system gives the compound  $C_7H_7OH$ ,  $C_6H_2(NO_2)_3OH$ , unstable at its maximum, m. p.  $65.6^\circ$  (by extrapolation). The freezing-point curve is given in the diagram on page 1313.

(a) Solid phase,  $C_6H_2(NO_2)_3OH$ .

% $C_6H_2(NO_2)_3OH$ .....	100	91.1	80.2	69.9	62.8	56.4	51.0
T.....	118.5	112.0	103.4	93.7	86.2	78.0	70.3

(b) Solid phase,  $C_7H_7OH$ ,  $C_6H_2(NO_2)_3OH$ .

% $C_6H_2(NO_2)_3OH$ .....	46.5	43.9	38.8	32.8	27.6	22.3	16.9	11.4
T.....	65.2	64.4	62.3	58.5	54.7	49.6	43.1	35.5

(c) Solid phase,  $C_7H_7OH$ .

% $C_6H_2(NO_2)_3OH$ .....	5.9	0
T.....	30.1	34.5

**14. Thymol-Picric Acid.**—The equimolecular addition compound  $C_{10}H_{13}OH$ ,  $C_6H_2(NO_2)_3OH$  was obtained, stable at its maximum; m. p.  $96.8^\circ$ .

(a) Solid phase,  $C_6H_2(NO_2)_3OH$ .

% $C_6H_2(NO_2)_3OH$ .....	100	89.8	81.1	75.4	69.3	62.5
T.....	118.5	113.0	108.0	105.0	102.0	99.8

(b) Solid phase,  $C_{10}H_7OH$ ,  $C_6H_2(NO_2)_3OH$ .

% $C_6H_2(NO_2)_3OH$ .....	53.5	51.5	47.0	42.0	36.7	32.5	28.1	22.8	16.6
T.....	96.0	96.6	96.1	94.2	91.6	89.2	86.3	81.1	71.9

(c) Solid phase,  $C_{10}H_7OH$ .

% $C_6H_2(NO_2)_3OH$ .....	3.2	0
T.....	48.2	49.6

15.  $\alpha$ -Naphthol-Picric Acid.—This system gives an addition product—probably  $C_{10}H_7OH$ ,  $C_6H_2(NO_2)_3OH$ —but the melting point of the compound is so high that mixtures containing more than a small amount of picric acid become very explosive, consequently the curve could not be determined.

### Consideration of Results.

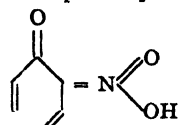
Of the thirteen phenols examined with picric acid in this and previous investigations, ten are found to give addition products, the three nitrophenols alone providing negative results.<sup>1</sup> This is again in accordance with the views advanced in the introductory section regarding the nature of the reaction, since the nitrophenols are the most highly acidic of all those investigated<sup>2</sup> and therefore exhibit the least tendency towards compound formation with a *strong* acid.

When the freezing-point curves of phenols with picric acid are compared with those given with trichloroacetic acid in an earlier section, it is seen that picric acid behaves as the stronger acid of the two. The maxima for the addition compounds with this acid are sharper throughout the whole series of curves in spite of the higher temperatures involved. Picric acid, also, gives addition products with the naphthols, which do not combine at all with trichloroacetic acid. The phenols thus resemble alcohol in being better dissociating media for picric acid than for trichloroacetic, although in aqueous solution the two acids are very nearly equally ionized. In the same way sulfuric acid, as will be evident from the table on page 1314, is a stronger acid than picric in phenol solutions, since it is capable of compound formation even with the nitrophenols. In aqueous solution the order is reversed.

Eight of the ten compounds obtained from systems of the type: weak phenol-picric acid are equimolecular.<sup>3</sup> The reaction for their formation may be expressed, in accordance with the arguments advanced previously,

<sup>1</sup> The system quinol-picric acid gives no compound owing to decomposition of the quinol (Philip and Smith, *J. Chem. Soc.*, 87, 1735 (1905)).

<sup>2</sup> *o*- and *p*-Nitrophenols (also picric acid) may well be stronger acids in the nitronic

forms, , than in the phenol forms. It is instructive to note that *m*-nitrophenol is a much weaker acid than its *o*- and *p*-isomers (see page 1312).

<sup>3</sup> The composition of the  $\alpha$ -naphthol-picric acid compound could not be determined.

by Equation II on page 1317. The compound of *m*-cresol with picric acid is peculiar in containing two molecules of *m*-cresol to one of acid.

### III. Systems: Weak Acid-Strong Phenol.

No previous work has been done upon systems of this class. The examples of this type investigated below gave only negative results, no compounds being isolated. The same is true of two systems of the type: weak acid-weak phenol, which are also recorded in the following tables:

#### 16. Acetic Acid-Picric Acid.—

(a) Solid phase,  $C_6H_3(NO_2)_3.OH$ .

% $C_6H_3(NO_2)_3.OH$ .....	100	76.0	63.6	53.5	45.0	35.9	25.3	17.0	12.5
T.....	118.5	106.5	100.1	94.9	90.0	84.7	76.7	65.1	55.1

(b) Solid phase,  $CH_3.COOH$ .

% $C_6H_3(NO_2)_3.OH$ .....	3.6	0
T.....	14.1	16.4

17. *o*-Toluic Acid-Picric Acid.—This system is shown in the diagram on page 1313.

(a) Solid phase,  $C_6H_3(NO_2)_3.OH$ .

% $C_6H_3(NO_2)_3.OH$ .....	100	88.2	75.1	64.5	54.9	44.1	35.0
T.....	118.5	113.5	108.0	103.8	99.2	94.9	90.3

(b) Solid phase,  $C_7H_7.COOH$ .

% $C_6H_3(NO_2)_3.OH$ .....	27.3	18.4	9.0	0
T.....	89.0	93.5	98.4	103.4

#### 18. *m*-Toluic Acid-Picric Acid.—

(a) Solid phase,  $C_6H_3(NO_2)_3.OH$ .

% $C_6H_3(NO_2)_3.OH$ .....	100	92.7	85.7	78.0	70.4	61.0	50.4	41.9	34.0
T.....	118.5	114.9	112.0	108.8	105.7	101.7	97.0	93.1	89.9

(b) Solid phase,  $C_7H_7.COOH$ .

% $C_6H_3(NO_2)_3.OH$ .....	27.8	20.0	10.2	0
T.....	90.2	96.0	102.5	109.6

#### 19. $\alpha$ -Toluic Acid-Picric Acid.—

(a) Solid phase,  $C_6H_3(NO_2)_3.OH$ .

% $C_6H_3(NO_2)_3.OH$ .....	100	91.1	79.7	67.5	56.3	45.0	35.1	23.3	13.2
T.....	118.5	114.6	109.7	104.9	100.0	95.2	90.0	82.7	74.0

(b) Solid phase,  $C_7H_7.COOH$ .

% $C_6H_3(NO_2)_3.OH$ .....	7.5	0
T.....	72.4	76.7

20. Phenol-Chloroacetic Acid.—No compound formation was observed between phenol and this moderately weak acid. (See diagram, page 1313.)

(a) Solid phase,  $CH_2Cl.COOH$ .

% $CH_2Cl.COOH$ .....	100	88.5	78.1	67.9	58.3	46.7	37.9
T.....	61.4	56.0	50.4	44.9	39.1	30.9	23.6

(b) Solid phase,  $C_6H_5OH$ .

% $CH_2Cl.COOH$ .....	30.0	18.5	8.8	0
T.....	17.4	27.1	35.1	42.4

21. *o*-Cresol-Chloroacetic Acid.—Here also no compound is indicated.

(a) Solid phase,  $CH_2Cl.COOH$ .

% $CH_2Cl.COOH$ .....	100	86.3	75.2	63.0	51.1	39.4	30.6
T.....	61.4	54.9	49.2	42.4	34.8	25.7	17.4

(b) Solid phase,  $C_7H_7OH$ .

% $CH_2Cl.COOH$ .....	27.6	17.9	8.6	0
T.....	16.7	21.8	26.6	30.4

## Consideration of Results.

None of the weak acids examined with picric acid in the above tables gave addition compound formation, and the freezing-point curves indicate that no compounds exist in solution. This is an unexpected result, since the same weak acids have been shown to form stable compounds with trichloroacetic acid<sup>1</sup> and with sulfuric acid.<sup>2</sup>

The conclusion must be drawn that the weak organic acids, unlike the phenols, are better dissociating media for trichloroacetic acid than for picric acid. Such differences of behavior, however, as have been noted here and in a preceding section do not deserve much emphasis, since the general results of work in this field indicate that, in cases of such weak combination, quite small variations in atidic strength are sufficient to induce or inhibit the isolation of compounds.

The two systems of the type: weak acid-weak phenol recorded above also gave no addition compounds, as was only to be expected from systems containing two components of not widely different acidic strengths. Similarly Paterno and Ampolla<sup>3</sup> found no compound formation in the systems thymol-acetic acid and thymol-phenol.

## Summary.

The examination of compound formation in two-component systems of the type: strong organic acid-weak organic acid has been completed by including phenols in the investigation. Systems of the general type: phenol-acid have been studied in which the acidic strengths of both components have been varied as widely as possible.

In accordance with the results of previous papers, it has been found that addition compounds are obtained only when the acidic strengths of the two components are very widely separated. Thus weak phenols give oxonium salts with a strong acid or a strongly acidic phenol (trichloroacetic acid or picric acid). A number of such compounds have been

<sup>1</sup> Kendall, *THIS JOURNAL*, 36, 1722 (1914).

<sup>2</sup> Kendall and Carpenter, *Ibid.*, 36, 2498 (1914).

<sup>3</sup> Paterno and Ampolla, *Gazz.*, 27, 481 (1897).



isolated and described. Systems containing components of not so widely divergent ædic strengths give no compound formation.

The reaction is assumed to be similar in its nature to those studied in previous papers, *i. e.*, the compounds are regarded as true oxonium salts. The equation may be written as follows:



This reaction probably represents the first stage in the formation of phenolic esters of organic acids. The further study of the mechanism of the esterification process will be the subject of a subsequent paper.

NICHOLS LABORATORIES OF INORGANIC CHEMISTRY,  
COLUMBIA UNIVERSITY, NEW YORK CITY.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI.]

## VI. FURTHER EVIDENCE FOR THE ELECTRONIC FORMULA OF BENZENE AND THE SUBSTITUTION RULE.<sup>1</sup>

By HARRY SHIPLEY FRY.

Received April 13, 1916.

In previous papers of this series<sup>2</sup> numerous facts have been presented and interpreted by means of the electronic formula of benzene (abbreviated formula, Fig. 1). A substitution rule was indicated maintaining that

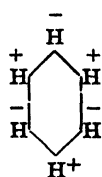


Fig. 1.

when substituents are of the same sign or polarity they will occupy positions which are meta to each other, but if two substituents are of opposite sign or polarity they will occupy either ortho or para positions to each other. This follows from the fact that the electronic formula of benzene is the only formula presenting conjointly a structural basis and an electronic interpretation of the relations between the ortho and para positions and substituents in contradistinction to the meta positions and substituents.

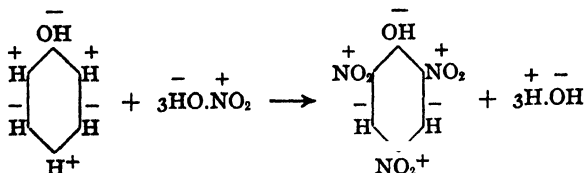
The purpose of the present paper is to present briefly additional experimental facts which further substantiate the electronic formula of benzene and the substitution rule. The facts here offered seem particularly significant since they involve polysubstituted derivatives of benzene.

Phenol, when directly nitrated, yields ortho- and para-nitrophenols. Further nitration yields the two isomeric 1,2,4- and 1,2,6-dinitrophenols.

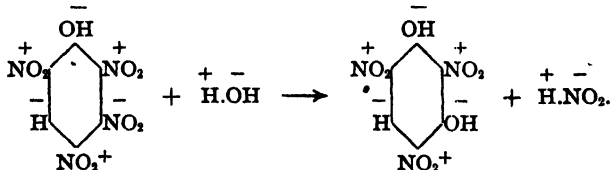
<sup>1</sup> This and the two following papers constitute Parts VI, VII, and VIII of the series, "Interpretations of Some Stereochemical Problems in Terms of the Electronic Conception of Positive and Negative Valences." Parts VI and VIII were read before the Cincinnati Section of the American Chemical Society, May 12, 1915.

<sup>2</sup> Fry, *THIS JOURNAL*, 36, 248, 262, 1035 (1914); *Ibid.*, 37, 855, 863, 883, 2368 (1915); see also Fry, *Z. physik. Chem.*, 76, 385, 398, 591 (1911); *Ibid.*, 80, 29 (1912); *Ibid.*, 82, 665 (1913); *Ibid.*, 90, 458 (1915).

Finally, nitration of either of these products gives the symmetrical trinitro derivative, picric acid. These reactions are summarized in the following electronic equation:<sup>1</sup>



In trinitrophenol each of the nitro groups is positive but the electronic formula indicates that in tetranitrophenol a fourth nitro group in position 3 or 5 would be negative. Now if some nitro groups are positive and others are negative there should be some marked difference in their behavior toward certain reagents. These conclusions are substantiated by the fact that "the nitro group in nitrobenzene is extremely stable compared with the fourth nitro group in tetranitrophenol, which water will remove in the form of nitrous acid."<sup>2</sup> These facts are in perfect agreement with the electronic formula of tetranitrophenol, the hydrolysis of which yields nitrous acid ( $\text{H}.\text{NO}_2$  or  $\text{H}.\text{ONO}$ )<sup>3</sup> according to the electronic equation



Since direct nitration with nitric acid results in the substitution of positive nitro groups and since in tetranitrophenol the negative nitro group may occupy either of the equivalent positions 3 or 5, with negative hydroxyl in position 1, it follows that substituents in positions 1, 3, and 5 are negative while those in positions 2, 4, and 6 are positive. This is a confirmation of the electronic formula of benzene and the substitution rule stated above.

In previous papers it has been shown that hydrogen-,<sup>4</sup> halogen-, hydroxyl-sulfonic,<sup>5</sup> and carboxyl-radicals<sup>6</sup> may function either positively or negatively, depending principally upon the relative positions they may occupy in the benzene nucleus. Now with reference to the existence of positive

<sup>1</sup> For detailed description of the mechanism of substitution, see Fry, *THIS JOURNAL*, 37, 875 (1915).

<sup>2</sup> Cohen, "Organic Chemistry," Vol. II, p. 90.

<sup>3</sup> For tautomeric and electronic formulas of nitrous acid see Fry, *THIS JOURNAL*, 37, 875 (1915) and *Z. physik. Chem.*, 90, 464 (1915).

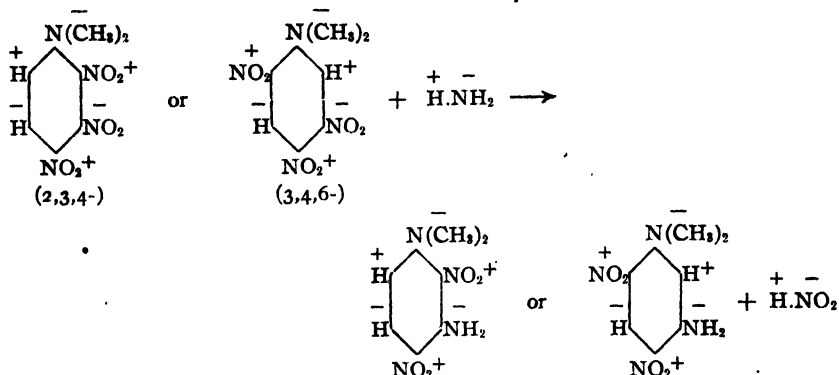
<sup>4</sup> Fry, *THIS JOURNAL*, 36, 262 (1914).

<sup>5</sup> *Ibid.*, 37, 864 (1915).

<sup>6</sup> *Ibid.*, 36, 256 (1914).



in the 2,4,6-compound the nitro groups in positions 4 and 6 are also regarded as positive since they are not replaced by  $\text{NH}_2$ . They occupy positions ortho- and para-, respectively, to the negative nitro group of position 3. All of these facts and conclusions are embodied in and interpreted by the following electronic formulas and equations:



In all benzene formulas positions 2 and 6 are equivalent as are also positions 3 and 5. Accordingly, the 2,3,4- and 3,4,6-trinitrodimethylanilines (and their products of interaction with ammonia) coincidentally show that when the substituents in positions 1, 3, and 5 are negative, the substituents in positions 2, 4, and 6 are positive. This also constitutes a further substantiation both of the electronic formula of benzene and the substitution rule.

Additional evidence leading to the above conclusions might be described in detail but brief mention may suffice. Michele Giua<sup>1</sup> and A. Contardi<sup>2</sup> have described a number of polynitro derivatives of benzene which suffer replacement of a nitro group by OH, O(CH<sub>3</sub>), NH<sub>2</sub> and NH(CH<sub>3</sub>) with the liberation of nitrites. In some instances hydrolysis with water yields nitrous acid anhydride. In these various instances two nitro groups are adjacent, *i. e.*, occupy positions ortho- to each other, and only one of them suffers replacement. Giua maintains that this behavior substantiates the rule on the reactivity of the nitro groups in the benzene ring proposed by Körner and Laubenheimer who attribute the facility of reaction of the one nitro group to the adjacency of the two nitro groups and the consequent "loosening" action of one group upon the other. This interpretation is not only vague but it fails to take into account the highly significant facts that the nitro group is replaced by a substituent of *negative polarity* and that the group thus replaced is liberated as a *nitrite* in which the *nitro radical is also negative*. The electronic conception of positive and

<sup>1</sup> *Atti accad. Linc-i*, 23, 484 (1914); *Gazz. chim. ital.*, 45, 339, 352 (1915).

<sup>2</sup> *Ibid.*, 23, 464 (1914).

negative valences and the existence of positive and negative nitro groups affords a more satisfactory interpretation, since all of the facts noted are indicated and correlated by the electronic formula of benzene and the substitution rule. Conversely, the facts verify the electronic formula of benzene and the substitution rule.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI.]

## VII. THE ACTION OF SODIUM METHYLATE UPON THE PRODUCTS OF NITRATION OF ORTHO-, PARA- AND META-CHLOROTOLUENES.

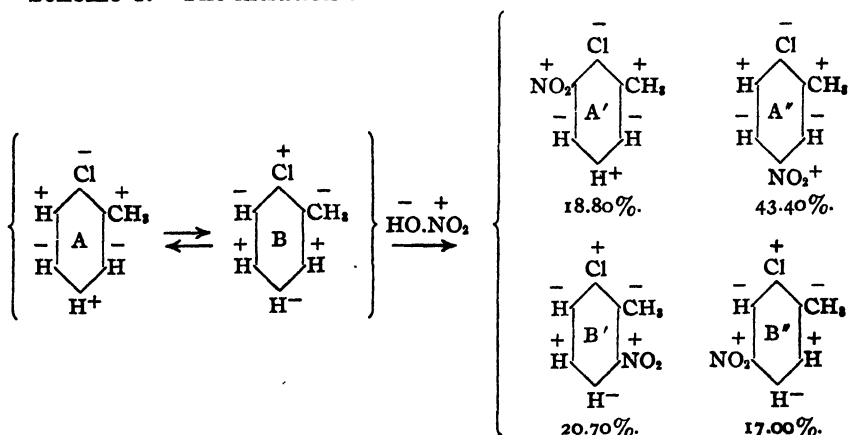
By HARRY SHIPLEY FRY.

Received April 13, 1916.

Part IV<sup>1</sup> of this series considered in detail the simultaneous formation of *o*-, *p*-, and *m*-substituted derivatives of benzene from the standpoint of the electronic tautomerism of benzene derivatives.<sup>2</sup> The present paper (VII) is a continuation of Part IV and embodies the results of a quantitative study of the action of sodium methylate solutions of various concentrations upon the products of nitration of *o*-, *p*-, and *m*-chlorotoluenes. The results of these experiments, in addition to the facts given in Part IV, are offered as further evidence for the electronic tautomerism<sup>3</sup> of certain substituted derivatives of benzene.

In order to follow the experimental part of this work it will be necessary to indicate briefly, from the standpoint of the conception of electronic tautomerism, the electronic equations for the nitrations of *o*-, *p*-, and *m*-chlorotoluenes according to the following Schemes 1, 2, and 3, respectively.

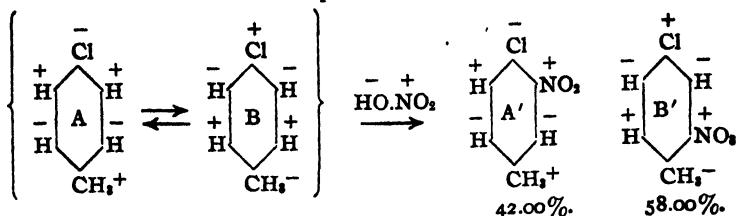
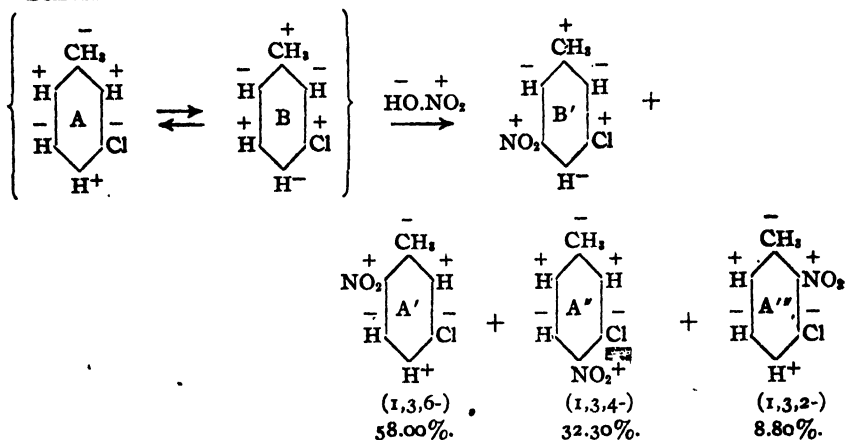
**Scheme 1.**—The nitration of *o*-chlorotoluene.



<sup>1</sup> Fry, *THIS JOURNAL*, 37, 863 (1915).

<sup>2</sup> Fry, *Z. physik. Chem.*, 76, 390 (1911); *THIS JOURNAL*, 37, 864 (1915).

<sup>3</sup> For a detailed account of the mechanism of the electronic tautomerism of benzene derivatives see Fry, *THIS JOURNAL*, 37, 873 (1915).

**Scheme 2.**—The nitration of *p*-chlorotoluene.**Scheme 3.**—The nitration of *m*-chlorotoluene.

The above schemes were the bases of the interpretations of the nitration reactions of Wibaut,<sup>1</sup> Holleman<sup>2</sup> and Wibaut,<sup>3</sup> respectively, who determined the percentage yields of the several isomers of each nitration by physical methods—processes of fractional crystallization and comparisons of curves of fusion of mixtures of unknown composition with those of known composition.

In each of these schemes it will be observed that the nitration products (A', A'', etc.) of the electromer A embody negative chlorine while those (B', B'', etc.) of electromer B embody positive chlorine. Now, if it be possible to show by quantitative chemical methods that the yields of the isomers (chloronitrotoluenes) which contain negative chlorine are commensurate with the yields of the same isomers ascertained by Holleman and Wibaut by physical methods, then the conception of the electronic tautomerism of the chlorotoluenes as indicated in Schemes 1, 2, and 3, is, in a measure, substantiated.

The chemical method for the determination of the yields of the isomers containing negative chlorine depends, first, upon the completeness of

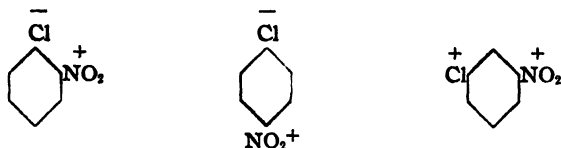
<sup>1</sup> *Recueil*, 32, 244 (1913).

<sup>2</sup> *Ibid.*, 28, 408 (1909).

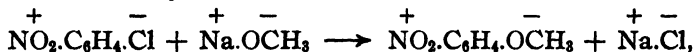
<sup>3</sup> *Ibid.*, 32, 244 (1913).

their interaction with sodium methylate and, second, the noninteraction of the isomers containing positive chlorine. In order to test the applicability of these two points, the action of sodium methylate in methyl alcohol solution upon *o*-, *p*-, and *m*-chloronitrobenzenes was investigated. These isomers were chosen because it is commonly recorded that the *o*- and *p*-isomers exchange their halogen atom for OH, O(CH<sub>3</sub>) or NH<sub>2</sub>, while the *m*-isomer is nonreactive.

An interpretation of these reactions has been given<sup>1</sup> from the standpoint of the electronic formula of benzene and the substitution rule. The abbreviated electronic formulas of the chloronitrobenzenes are as follows:



Only those isomers containing negative halogen (*o*- and *p*-) should interact with sodium methylate, thus,



and the *m*-isomer, containing positive chlorine, should be nonreactive under the same conditions.

The extent of the replacement of negative chlorine can be found by determining the quantity of sodium chloride liberated. After repeated experiments, designed to secure the conditions noted, the following method was found to yield theoretical results: About 0.2 g. of the chloronitrobenzene was dissolved in 15 cc. of a normal solution of sodium methylate in absolute methyl alcohol. The solution was heated in a sealed glass tube for 5 hours at 100°. The contents of the tubes were then diluted to a volume of 200 cc., acidified with nitric acid, boiled to expel the methyl alcohol, cooled, and filtered. The quantity of sodium chloride in the respective filtrates was determined by titration with standard solution of silver nitrate. The following results were obtained:

Substance.	(Grams.)	No. cc. 0.9957 N AgNO <sub>3</sub> solution.	% negative Cl. Found.	% negative Cl. Theor.
$\text{O-Cl.C}_6\text{H}_4\text{.NO}_2$ .....	0.2005	12.81	22.56	22.51
$\text{P-Cl.C}_6\text{H}_4\text{.NO}_2$ .....	0.2007	12.78	22.48	22.51
$\text{m-Cl.C}_6\text{H}_4\text{.NO}_2$ .....	0.1992	00.00	00.00	00.00

These results show that isomers containing negative chlorine may be estimated quantitatively, provided conditions are secured for their complete interaction with sodium methylate, while under the same conditions the isomer containing positive chlorine is nonreactive.

<sup>1</sup> Fry, Z. *physik. Chem.*, 76, 395 (1911); THIS JOURNAL, 36, 253 (1914).

The chief problem of the present investigation was to secure conditions under which the negative halogen atoms of the nitration products of *o*-, *p*-, and *m*-chlorotoluenes would completely interact with sodium methylate and thus afford a chemical method for determining the percentage yields of the isomers of chloronitrotoluene which contain negative chlorine. A comparison of the chemically determined and the physically determined yields could then be made. With this end in view, *o*-, *p*-, and *m*-chlorotoluenes were each separately nitrated (at 0°) according to the specific directions given by Wibaut, Holleman and Wibaut, respectively.<sup>1</sup> The methods were originally designed to yield only mononitro substitution products. The respective products of nitration of each of the chlorotoluenes, which consisted of mixtures of the different isomers (nitrochlorotoluenes), as indicated in the preceding Schemes 1, 2, and 3, were treated with sodium methylate solutions of varying concentrations—0.5 *N*, *N*, 2 *N* and 3 *N*. Samples, 0.2 to 0.4 g., of the nitration products were heated, each with 15 cc. of the sodium methylate solution in sealed tubes, for 10 hours at 100°. The contents of the tubes were then analyzed, as previously described, for the negative chlorine, liberated as  $\text{Na}^+\text{Cl}^-$ , precipitated and weighed as silver chloride. The percentage yield of the combined isomers containing negative chlorine was calculated from the ratio  $\text{Ag}^+\text{Cl}^- : \text{Cl}^-\text{NO}_2\text{CH}_3\text{C}_6\text{H}_5$ . The results of these experiments are recorded in three sections (I, II and III) to correspond with Schemes 1, 2, and 3 for the nitration of *o*-, *p*-, and *m*-chlorotoluenes, respectively. All reactions were conducted in duplicate.

TABLE I.

I. Action of Sodium Methylate upon the Isomers Derived from *o*-Chlorotoluene. (See Scheme 1.)

Mixture of isomers (gram).	Normality NaOCH <sub>3</sub> .	AgCl (gram).	% yield of isomers A' + A'', 1,2,6- and 1,2,4-Cl, CH <sub>3</sub> , NO <sub>2</sub> , C <sub>6</sub> H <sub>5</sub> .			Average.
			1,2,6-	1,2,4-	Average	
0.2625	0.5 <i>N</i>	0.1163		53.01		
0.2434	0.5 <i>N</i>	0.1084		53.29		53.15
0.2835	<i>N</i>	0.1388		58.58		
0.2938	<i>N</i>	0.1446		58.89		58.73
0.3283	2 <i>N</i>	0.1362		49.64		
0.2994	2 <i>N</i>	0.1254		50.12		49.83
0.2772	3 <i>N</i>	0.0884		38.16		
0.2940	3 <i>N</i>	0.0941		39.30		38.23

These results indicate that the extent of the reaction with sodium methylate is greatest in the normal solution. A 58.73% yield of the combined isomers containing negative chlorine was obtained. The yields of these isomers determined by the physical methods of Wibaut<sup>1</sup> totals 62.20%.

<sup>1</sup> *Loc. cit.*



The yields obtained by the two methods, while not identical, approximate closely. Variations will be considered later.

TABLE II.

II. Action of Sodium Methylate upon the Isomers Derived from *p*-Chlorotoluene. (See Scheme 2.)

Mixture of isomers (gram).	Normality NaOCH <sub>3</sub>	AgCl (gram).	% yield of isomer A', 1,2,4-Cl, NO <sub>2</sub> , CH <sub>3</sub> , C <sub>6</sub> H <sub>5</sub> .	Average.
			— + +	
0.2707	0.5 <i>N</i>	0.0799	35.33	
0.2868	0.5 <i>N</i>	0.0842	35.13	35.23
0.3068	<i>N</i>	0.0946	36.89	
0.2608	<i>N</i>	0.0773	35.47	36.18
0.2854	2 <i>N</i>	0.0750	31.44	
0.3068	2 <i>N</i>	0.0780	30.42	30.93
0.3297	3 <i>N</i>	0.0814	29.54	
0.3037	3 <i>N</i>	0.0769	30.30	29.92

Here also the extent of the reaction with sodium methylate was greatest in the normal solution, which indicated a yield of 36.18% of the isomer containing negative chlorine. The yield of the same isomer determined by Holleman (fusion curve method) was 42.00%.

TABLE III.

III. Action of Sodium Methylate upon the Isomers Derived from *m*-Chlorotoluene. (See Scheme 3.)

Mixture of isomers (gram).	Normality NaOCH <sub>3</sub>	AgCl (gram).	% yield of isomers A' + A'' + A''', 1,3,6- + 1,3,4- + 1,3,2-CH <sub>3</sub> , Cl, NO <sub>2</sub> , C <sub>6</sub> H <sub>5</sub> .	Average.
			— + +	
0.2257	0.5 <i>N</i>	0.1652	87.59	
0.2510	0.5 <i>N</i>	0.1843	87.86	87.77
0.2672	<i>N</i>	0.1987	88.99	
0.2520	<i>N</i>	0.1853	87.99	88.49
0.2670	2 <i>N</i>	0.1898	85.06	
0.3212	2 <i>N</i>	0.2308	85.98	85.52
0.2809	3 <i>N</i>	0.1923	81.92	
0.2808	3 <i>N</i>	0.1888	80.46	81.19

Again the extent of the reaction was greatest in the normal solution indicating a yield of 88.49% of the three isomers containing negative chlorine. Wibaut (fractional crystallization and fusion curve methods) obtained a 100% yield of these isomers.

The yields of the isomers containing negative chlorine determined by physical methods and the maximum yields of the same isomers determined by chemical methods are summarized in the following table:

TABLE IV.

Scheme.	Isomers.	Physical.	Chemical.	% Ratio.
1.....	(A' + A'')	62.20 (Wibaut)	58.73 (Fry)	94.42
2.....	(A')	42.00 (Holleman)	36.18 (Fry)	86.14
3.....	(A' + A'' + A''')	100.00 (Wibaut)	88.49 (Fry)	88.49

The extreme care with which Holleman and Wibaut conducted their physical determinations leads one to accept their results as practically final. Accordingly, in the last column above, the chemically determined yields are recorded as percentages of the physically determined yields. If each of the values in the last column was 100% then it might be assumed without question that the conception of the electronic tautomerism of the *o*-, *p*-, and *m*-chlorotoluenes given in Schemes 1, 2, and 3, respectively, is completely substantiated. Without making this assumption or claim it may, nevertheless, be maintained that in so far as the values in the last column do approach the theoretical, so far do they substantiate the electronic tautomerism of the chlorotoluenes. Moreover, it may be said that the electronic tautomerism of *o*-, *p*-, and *m*-chlorotoluenes is the only hypothesis that has accounted for the replaceability of certain halogen atoms in some of the isomeric nitrochlorotoluenes and the nonreplaceability of certain halogen atoms in others. The data presented in this paper substantiate the hypothesis.

The fact that the chemically determined quantities of the isomers containing negative chlorine were less than the quantities determined by physical methods may have been due to two causes. First, the interaction with sodium methylate of one or more of these isomers in the mixtures may have been incomplete. This is not likely, since the results of the experiments with the analogous chloronitrobenzenes gave results in perfect agreement with the theory. Furthermore, a survey of the quantitative data given in connection with Schemes 1, 2, and 3 shows a maximum replacement in every reaction in which the uninormal solutions of sodium methylate were used. Concentrations below or above normal gave lower yields.

In the second place, the low yields of the isomers containing negative chlorine may be due to the fact that the relative quantities of the isomers obtained on nitration of the chlorotoluenes in Holleman's laboratories may not have been identical with the relative quantities of the same isomers obtained in this laboratory, even though the original directions given by Holleman and Wibaut were carried out precisely. The variations are most likely due to lack of standardization in certain details of manipulation, such as the rate of the addition of the nitric acid, methods of stirring, cooling, etc. While the temperature variations were kept within the prescribed limits, primarily to avoid the formation of polynitro derivatives, it is quite likely that the local temperature effects in the reaction mixture may have altered the relative quantities of the isomers formed. In fact, when nitrations were conducted separately, but under identical conditions, variations in the fusion points of the resulting mixtures were noted. This signifies corresponding variations in the relative quantities of the isomers in these mixtures.

In conclusion, the variations between the chemically and the physically determined yields are not sufficient to invalidate the principle of the electronic tautomerism of the chlorotoluenes. The conception affords a consistent interpretation of the observed facts and is substantiated in a great measure by the quantitative data offered in this paper. In the following paper (Part VIII) the conception of electronic tautomerism is developed further and confirmed more completely.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI.]

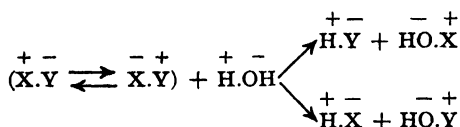
### VIII. FURTHER EVIDENCE FOR THE ELECTRONIC TAUTOMERISM OF BENZENE DERIVATIVES.<sup>1</sup>

By HARRY SHIPLEY FRY.

Received April 13, 1916.

The purpose of the present paper is to consider certain experimental facts, the interpretation of which fully warrants the assumption of the existence of electromers in dynamic equilibrium, *i. e.*, electronic tautomerism. Quantitative data will also be presented which conclusively confirm the principle of electronic tautomerism. A few underlying principles should be recalled.

Hydrolysis reactions commonly constitute an experimental method<sup>2</sup> for designating the polarity of the radicals of a compound under the particular conditions of hydrolysis. The following general scheme embodies the theoretical and the actual possibilities presented by hydrolysis reactions:



If the compound in question, XY, on hydrolysis yields only H.Y and HO.X, then XY is qualified by the electronic formula  $\overset{+}{X}-\overset{-}{Y}$ , or  $\overset{+}{X}.Y$ . If, on the other hand, conditions are such that hydrolysis yields only H.X and HO.Y, then XY is qualified by the formula  $\overset{-}{X}.Y$ . In some reactions the four possible products are obtained and, accordingly, the compound XY presents an illustration of electronic tautomerism, *i. e.*, the existence of both electromers  $\overset{+}{X}.Y \rightleftharpoons \overset{-}{X}.Y$  in dynamic equilibrium. A number of instances<sup>3</sup> has been recorded, in which reactions proceed

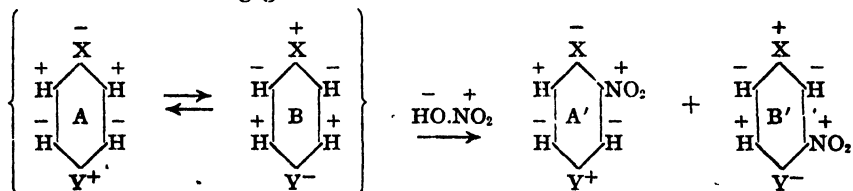
<sup>1</sup> Read before the Cincinnati Section of the American Chemical Society, May 12, 1915.

<sup>2</sup> Fry, *Z. physik. Chem.*, 76, 395 (1911); W. A. Noyes, *THIS JOURNAL*, 23, 460 (1901) and Stieglitz, *THIS JOURNAL*, 23, 796 (1901) were the first to employ hydrolysis reactions as a means of indicating the polarities of the radicals of substances.

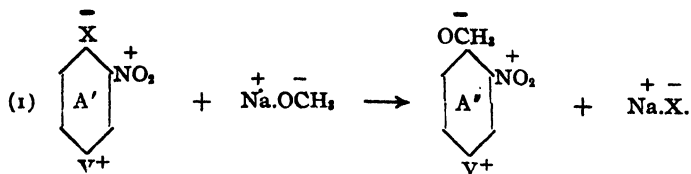
<sup>3</sup> Fry, *THIS JOURNAL*, 37, 864 (1915); L. W. Jones, *Am. Chem. J.*, 50, 414 (1913).

according to the above and analogous schemes, and therefore substantiate the existence of electromers and electronic tautomerism. Particularly significant, in this connection, are the nitrations of the mixed dihalogen benzenes and the subsequent hydrolyses of their nitration products with sodium methylate. Some remarkable consequences may now be predicted if we consider the mixed dihalogen benzenes from the standpoint of the electronic formula of benzene and the principle of electronic tautomerism.

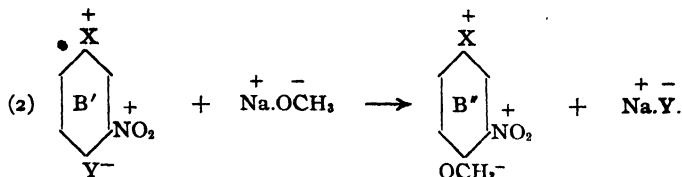
When two substituents occupy positions either ortho or para to each other they are of opposite polarity. Hence in the electronic formula for a *p*-dihalogen benzene in which the halogen atoms X and Y are different chemically, it follows that if X is negative, Y is positive; or, if X is positive, Y is negative. Now, in the nitration of a *p*-disubstituted derivative of benzene only two mononitro substitution products are possible, and, from the standpoint of the principle of electronic tautomerism as applied to a *p*-dihalogen benzene, the nitration reaction should conform to the following general scheme:



If the principles underlying this general<sup>a</sup> scheme are correct, then certain definite consequences follow which should lend themselves to verification by experiment. What are some of these consequences? If the electromers of  $\text{C}_6\text{H}_4\text{XY}$  (designated as A and B) are in tautomeric equilibrium and if each electromer interacts with nitric acid, the respective isomers, A' and B', should be formed. Note particularly that in the isomer A', X is negative and Y is positive, while in isomer B', X is positive and Y is negative. In view of the facts presented in the preceding paper, notably the action of sodium methylate upon *o*-, *p*-, and *m*-chloronitrobenzenes, it follows that isomer A' on interaction with sodium methylate ( $\text{Na}\cdot\text{OCH}_3$ ) should exchange X for  $\text{OCH}_3$  and liberate  $\text{Na}\cdot\text{X}$  according to Equation 1.

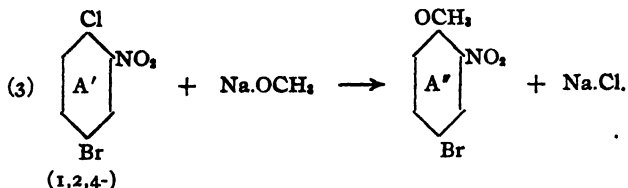


On the other hand, isomer B' should exchange  $\text{Y}^-$  for  $\text{OCH}_3^-$  and liberate  $\text{Na}\cdot\text{Y}$  according to Equation 2:



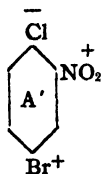
Furthermore, if electromers A and B are in tautomeric equilibrium and nitration yields a mixture of isomers A' and B' then the action of sodium methylate upon this mixture should yield not only the oxymethyl derivatives, A'' and B'', (Equations 1 and 2, respectively) but also a mixture of the sodium halides,  $\overset{+}{\text{Na}}.\overset{-}{\text{X}}$  and  $\overset{+}{\text{Na}}.\overset{-}{\text{Y}}$ . An experimental verification of these predictions would lead to a very definite conclusion, namely, that the *para* mixed dihalogen compound,  $\text{C}_6\text{H}_4\text{XY}$ , affords an example of electronic tautomerism. Otherwise it would be difficult, if not impossible, to account for the simultaneous formation of the halides,  $\overset{+}{\text{Na}}.\overset{-}{\text{X}}$  and  $\overset{+}{\text{Na}}.\overset{-}{\text{Y}}$ , when sodium methylate interacts with the products of nitration of the mixed dihalogen benzene.

Experimental facts will now be considered which are completely in agreement with the principles and general reactions just postulated. Holleman<sup>1</sup> and Heineken have made a thorough study of the nitration (at 0°) of various mixed dihalogen benzenes. For the present, attention will be confined to the nitration of *p*-chlorobromobenzene, which gave a mixture of the isomers 1,2,4- and 1,3,4-chloronitrobromobenzenes. In developing a quantitative chemical method for determining the yields of these isomers in the nitration mixture, Holleman found that the 1,2,4-isomer heated with 0.35 *N* sodium methylate solution in a sealed tube for five hours at 80° gave practically complete displacement of chlorine as sodium chloride while the bromine remained intact. The reaction proceeded quantitatively (98.40%) according to Equation 3.



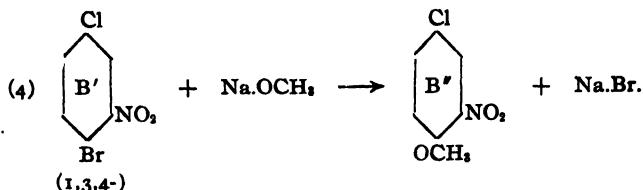
Note that this reaction is perfectly analogous to Equation 1, given above, in which  $\overset{-}{\text{X}}$  may now be  $\overset{-}{\text{Cl}}$ , and  $\overset{+}{\text{Y}}$  may be Br. The liberated sodium halide is  $\overset{+}{\text{Na}}.\overset{-}{\text{Cl}}$ . In other words, the 1,2,4-isomer (A') has the electronic formula

<sup>1</sup> *Recueil*, 34, 204 (1915).

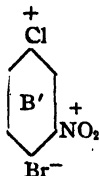


otherwise the liberation of chlorine as Na.Cl is inexplicable.

On the other hand, the 1,3,4-isomer on interaction with sodium methylate (under identical conditions) suffered *practically complete displacement of bromine as sodium bromide while the chlorine atom remained intact*. The reaction proceeded quantitatively (98.00%) according to Equation 4.

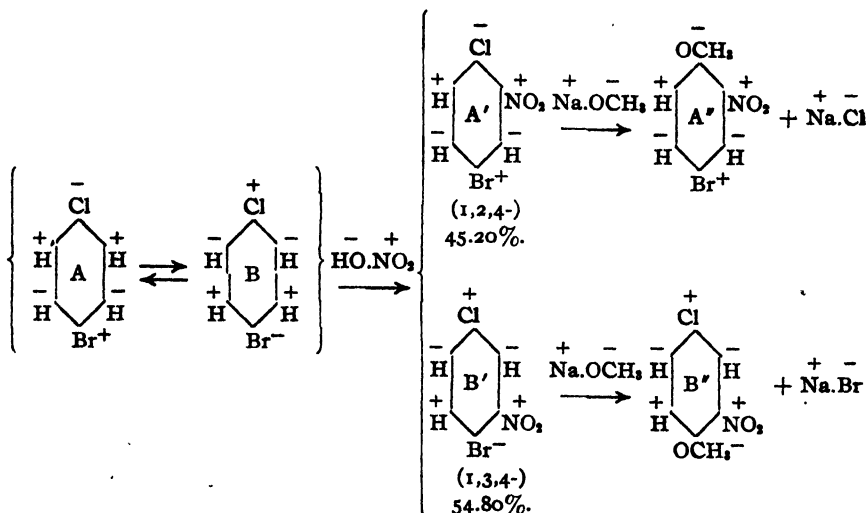


Note that this reaction is perfectly analogous to Equation 2 above, in which  $\overset{+}{\text{X}}$  may now be  $\overset{+}{\text{Cl}}$ , and  $\overset{-}{\text{Y}}$  may be  $\overset{-}{\text{Br}}$ . The liberated sodium halide is Na.Br. In other words, the 1,3,4-isomer (B') has the electronic formula



otherwise the liberation of bromine as Na.Br is inexplicable.

The quantitative interaction of 1,2,4- and 1,3,4-chloronitrobromobenzene with sodium methylate enabled Holleman to determine the relative quantities of these isomers obtained on nitrating *p*-chlorobromobenzene. The sodium chloride and sodium bromide liberated were precipitated as silver chloride and bromide. An analysis of the mixed precipitates gave the percentage yields of the isomers calculated upon the ratios AgCl: 1,2,4-isomer, and AgBr: 1,3,4-isomer. These calculations were based upon Equations 3 and 4 which are perfectly analogous to the preceding electronic Equations 1 and 2, respectively. The yields of the isomers were 45.20% and 54.80%, respectively. The complete correlation of all of these reactions with the electronic formulas and the principle of electronic tautomerism is embodied in the following scheme:



Now a survey of the above scheme shows that those molecules of 1,4-chlorobromobenzene which interact with nitric acid to give the 1,2,4-isomer, which in turn exchanges its *chlorine* atom for  $\text{OCH}_3$  and yields *sodium chloride*, cannot be identical with the molecules of 1,4-chlorobromobenzene which interact with nitric acid to give the 1,3,4-isomer, which in turn exchanges its *bromine* atom for  $\text{OCH}_3$  and yields *sodium bromide*. In other words, the 1,2,4-isomer (A'), containing  $\text{Cl}^-$  and  $\text{Br}^+$ , must be derived from molecules of 1,4-chlorobromobenzene which also contain  $\text{Cl}^-$  and  $\text{Br}^+$ , i. e., electromer A; and the 1,3,4-isomer (B'), containing  $\text{Cl}^+$  and  $\text{Br}^-$ , must be derived from molecules of 1,4-chlorobromobenzene which also contain  $\text{Cl}^+$  and  $\text{Br}^-$ , i. e., electromer B. Thus the existence of two types of molecules of 1,4-chlorobromobenzene, namely electromers A and B, is conclusively indicated. Their simultaneous interaction with nitric acid indicates tautomeric equilibrium. The relative yields of the isomers A' and B' are functions of the speeds of interaction of nitric acid with the respective electromers A and B, and, as shown in a previous paper,<sup>1</sup> the speeds of interaction are intimately related to the concentrations of the respective electromers in the reaction mixture.

It will not be necessary to extend this paper by giving similarly detailed descriptions of the nitrations of other mixed dihalogen benzenes,<sup>2</sup> since each example conforms perfectly to the schemes and principles presented in this and preceding papers. In conclusion, it is maintained

<sup>1</sup> See Parts III and IV of this series (Fry, *Loc. cit.*).

<sup>2</sup> *p*-Fluorochloro-, *p*-fluorobromo-, *p*-chloroiodo-, *o*-chlorobromo-, *o*-chloroiodo-, and *o*-bromoiodo benzene.

that each of these cases further substantiates the principle of electronic tautomerism or the existence of electromers in dynamic equilibrium.<sup>1</sup>

CINCINNATI, O.

[CONTRIBUTION FROM THE ORGANIC CHEMICAL LABORATORY OF THE STATE UNIVERSITY OF IOWA.]

## 4-NITRO-5-METHYL-2-SULFOBENZOIC ACID AND SOME OF ITS DERIVATIVES.

BY WILLIAM J. KARSLAKE AND PERRY A. BOND.

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In an earlier paper<sup>2</sup> we have shown that when 6-nitro-1,3-dimethylbenzene-4-sulfonic acid is oxidized by potassium permanganate in very dilute potassium hydroxide solution, three main products are formed, to wit, 6-nitro-3-methyl-4-sulFOBenzoic acid, 4-nitro-5-methyl-2-sulFOBenzoic acid and 6-nitro-4-sulfoisophthalic acid. Sometime later, Karslake and Huston<sup>3</sup> made derivatives of 6-nitro-3-methyl-4-sulFOBenzoic acid. The present work was undertaken to complete our knowledge of the second of these three acids.

In our previous work, 4-nitro-5-methyl-2-sulFOBenzoic acid was obtained in the form of the neutral potassium salt as the first crop of crystals from the oxidized nitro-xylene sulfonic acid. Analyses of this salt were persistently low in potassium. Since then it has been found that this first crop of crystals is usually contaminated with unoxidized 6-nitro-1,3-dimethylbenzene-4-sulfonic acid in the form of the potassium salt. The separation was accomplished finally by systematic fractional crystallization, the crystals being filtered off first from the fairly concentrated solution at 50°, and then from the cold, somewhat diluted filtrate after stand-

<sup>1</sup> Any objection to the use of the conception of electronic tautomerism on the grounds that electronic isomers (electromers) have not as yet been isolated is unwarranted because the conception of tautomerism, both in its historical and practical aspects, neither involves nor demands the immediate possibility of the isolation of the tautomers. In 1885, Laar (*Ber.*, 18, 648 (1885)), in a paper "Ueber die Möglichkeit mehrerer Strukturformeln für dieselbe chemisch Verbindung," defined tautomerism as the phenomenon of one substance doing duty for two structural isomers, *but the isolation of dynamic isomers or desmotropes was not effected until 1893*, the earliest examples being acetyldibenzoylmethane, tribenzoylmethane, and mesityloxide-oxalic ester described by Claisen (*Ann.*, 277, 183 (1893); 291, 25 (1896)). Strictly speaking, the term *tautomeric* is now applied to substances in which *only the equilibrium mixture of the structural isomers is known*; the term *desmotropic* is employed in cases where the isomers have been shown to be capable of independent existence. (Clarke, "Organic Chemistry," p. 251) The existence of electromers in dynamic equilibrium has been conclusively indicated. Their isolation as *electronic desmotropes* has not as yet been effected. Further discussion of this phase of the subject is reserved for future papers.

<sup>2</sup> THIS JOURNAL, 31, 405 (1909).

<sup>3</sup> *Ibid.*, 31, 1057 (1909).



ing several hours. The products thus obtained were recrystallized with due attention to temperature and concentration, until a complete separation was effected. About one hundred separate crystallizations were made in purifying the 235 grams of potassium salt used as a basis for this research. The influence of the impurity has very definite effects, and its removal was a necessity, as will be seen especially in the preparation of the acid chlorides. Analyses of the purified potassium salt, while slightly low, are much better than before.

Calc. for  $C_8H_5O_7NSK_2$ : K, 23.21. Found: K, 22.95, 23.01.

The **Neutral Lead Salt**,  $C_8H_5O_7NSPb + 3H_2O$ , was prepared by adding slightly more than the calculated amount of lead nitrate to the water solution of the potassium salt. It crystallizes quickly from moderately concentrated solution in fine crystals, which in some cases form leaf-like groups. Lead was determined by direct ignition in the crucible as the sulfate.

Calc. for Pb, 39.8;  $H_2O$ , 10.38. Found: Pb, 39.45;  $H_2O$ , 10.00.

The **Acid Potassium Salt**,  $C_8H_5O_7NSK + H_2O$ , was prepared in two ways: either by precipitating the silver from the silver potassium salt by dilute hydrochloric acid, evaporating and crystallizing; or by recrystallizing the neutral potassium salt from very concentrated hydrochloric acid. In the latter case, unless the hydrochloric acid is strong in the solution, the neutral potassium salt crystallizes out again, probably on account of its lesser solubility in water. The acid potassium salt once formed, however, can be recrystallized from water without decomposition. It comes out of the solution in beautiful, fine needles containing one molecule of water of crystallization.

Calc. for K, 12.33; acid hydrogen, 0.315;  $H_2O$ , 5.67.

Found: K, 11.81, 11.92; acid hydrogen, 0.317;  $H_2O$ , 5.74.

The **Free Acid**,  $C_8H_5O_7NS + 3H_2O$ , was prepared from the pure neutral silver salt by adding just a trifle more than the calculated amount of 0.1 *N* hydrochloric acid to the water solution of the salt, boiling, filtering, and evaporating to a small volume. The acid crystallized from water in plate-like needles strongly rosetted and easily broken. It had only a slight yellowish tint. It was insoluble in ether, ligroin, and carbon tetrachloride. It was soluble in acetone, ethyl acetate, or glacial acetic acid. Its melting point when it was crystallized from acetone or alcohol was  $94^\circ$ . The acid was titrated with sodium hydroxide, using phenolphthalein as the indicator.

Calc. for N, 4.44; acid hydrogen, 0.635;  $H_2O$ , 17.14.

Found: N, 4.45; acid hydrogen, 0.626;  $H_2O$ , 17.22.

**The Acid Chlorides.**—It was formerly stated<sup>1</sup> that the treatment of the

<sup>1</sup> *Loc. cit.* (Karslake and Bond).

potassium salt of the 4-nitro-5-methyl-2-sulfobenzoic acid with phosphorus pentachloride in a flask with reflux condenser at boiling temperature produced an oily substance which solidified with difficulty, but on being dissolved in carbon tetrachloride, dried, and partly evaporated, gave two products, one melting at  $133^{\circ}$ , the other an oily substance for which a melting point of  $93^{\circ}$  was suggested. It had been the experience of others<sup>1</sup> that the low-melting and high-melting chlorides crystallized in a constant melting mixture which had a lower melting point than that of the low-melting chloride. The two were separated in these cases by distilling in a vacuum.

The formerly observed melting point for the high melting chloride is approximately correct, the new value adopted being  $134^{\circ}$ , but now it has been definitely shown that the low melting point acid chloride melts at  $83^{\circ}$ , and is not involved as the prime cause of the oily mixture. In this case, as distinguished from the experience of others, no oil was produced when pure initial potassium salt was used, the two chlorides crystallizing out in absolutely distinct crystalline form. They were separated by fractional crystallization, and the symmetrical, high-melting chloride showed a tendency toward the formation of supersaturated solutions in carbon tetrachloride, the solvent used for the purification. The oily mass formerly found was, however, reproduced by mixing with the low-melting acid chloride, a portion of the acid chloride of the unoxidized nitro-xylene sulfonic acid. Its source in that work was evidently the impurity mentioned at the beginning of this paper.

**Symmetrical Acid Chloride,**  $\text{NO}_2.\overset{4}{\text{CH}_3}.\overset{5}{\text{C}_6\text{H}_2}.\overset{2}{\text{SO}_2}\overset{1}{\text{Cl.COCl}}$ .—The symmetrical acid chloride was formed in the largest amounts when the potassium salt of the acid was treated with phosphorus pentachloride in an open dish at the temperature of the steam bath, the ratio of the symmetrical to the unsymmetrical acid chloride thus formed being about three to five, and the total yield reaching 75% of the theoretical.

When the heating had caused complete liquefaction of the mass in the open dish, it was removed from the steam bath and poured into cold water. Phosphorus oxychloride and any phosphorus pentachloride remaining were dissolved in the water, and after a time the oil hardened. It was broken up with a stirring rod and ground with fresh water in a mortar. Finally the powder was let stand in more water over night, filtered, and the solid dried over sulfuric acid in a desiccator. It was next dissolved in hot carbon tetrachloride, filtered, and let stand to crystallize. If the solution was concentrated, the unsymmetrical chloride crystallized first and later there were superimposed on the crystalline mass hard, glistening, rhombohedral crystals of the symmetrical chloride. These

<sup>1</sup> Remsen, *Am. Chem. J.*, 30, 247 (1903); List and Stein, *Ber.*, 31, 1648 (1898).

were picked out by hand from the mass. In another experiment it was found that this chloride crystallized in the form of long, white needles. Once these were produced in the laboratory, the rhombohedral forms never appeared again. The needles seemed to be less soluble than the unsymmetrical acid chloride, and hence could be taken out from the carbon tetrachloride solution as the first crop of crystals. In some cases the solution was seeded to bring about the rapid production of this form.

The identity of the two crystalline forms of the symmetrical acid chloride was shown by the identical melting points,  $134^{\circ}$ , and also by the fact that when the rhombohedral form was dissolved in carbon tetrachloride and a trace of the needles added, the whole amount present crystallized out in the needle form.

The symmetrical acid chloride was recrystallized from carbon tetrachloride several times until the melting point was constant at  $134^{\circ}$ , and then analyzed.

Calc. for Cl, 23.80; N, 4.70; S, 10.74. Found: Cl, 23.65, 24.02; N, 4.68, 4.64; S, 10.72.

**Unsymmetrical Acid Chloride,**  $\text{NO}_2\text{CH}_2\text{C}_6\text{H}_2$   $\begin{cases} \text{C} = \text{Cl}_2(1) \\ > \text{O} \\ \text{SO}_2(2) \end{cases}$ .—This acid

chloride constituted about five-eighths of the total yield of the acid chlorides as made by the open dish method. Its formation is apparently favored by the presence of phosphorus oxychloride, for when a reflux condenser is used in the preparation of the chlorides, and the condensed phosphorus oxychloride formed is kept in the mixture, a much larger percentage of the unsymmetrical chloride is produced, although the absolute yield seems to be smaller. Holmes<sup>1</sup> used phosphorus oxychloride in sealed tubes for the preparation of the pure unsymmetrical acid chloride of *p*-nitro-*o*-sulFOBenzoic acid. In this case we found it not necessary, and the shorter process was used.

The purification of the unsymmetrical acid chloride by fractional crystallization from carbon tetrachloride was not difficult. It crystallized in short, tufted, rather soft needles, yellowish in color. An attempt was made to use the method of List and Stein<sup>2</sup> for the purification of the acid chlorides by distillation *in vacuo*. It was expected that the symmetrical chloride would decompose at the distillation temperature, while the unsymmetrical would distil unchanged. Distillation took place at the following temperatures and pressures:

Pressure in mm. mercury.....	21	11	10
Boiling point.....	218–220°	214°	212°

No difference was observed in the melting point of the pure  $83^{\circ}$  melting point substance by the distillation.

<sup>1</sup> *Am. Chem. J.*, 25, 204 (1901).

<sup>2</sup> *Ber.*, 31, 1648 (1898).

The acid chloride melting at  $83^{\circ}$  was analyzed, the methods used being the same as in the case of the high melting chloride.

Calc. for Cl, 23.80; N, 4.70; S, 10.74.

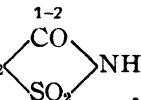
Found: Cl, 23.3, 23.4, 23.46; N, 4.82, 4.79; S, 10.77.

### Derivatives Obtained by the Action of Ammonia on the Acid Chlorides.

**A. From the Symmetrical Acid Chloride.**—A suitable amount of the acid chloride was placed in an open beaker and treated with concentrated ammonia. Apparently there was no action in the cold, but on raising the temperature slowly to boiling, so as to keep the concentration of the ammonia as high as possible, the acid chloride dissolved. When the excess of ammonia was evaporated off and the residue was cooled somewhat, the ammonium salt of the imide crystallized out as small glistening cubes. These were recrystallized from water several times. They then gave a melting point, with decomposition, of  $310-320^{\circ}$ . No other substance was recovered in the preparation except the ammonium chloride formed in the reaction. The symmetrical acid chloride is only slightly acted upon in nonaqueous solutions by ammonia.

Calc. for  $C_8H_9O_6N_3S$ : Total N, 16.21; Ammon. N, 5.40; S, 12.35.

Found: Total N, 16.20, 16.18; Ammon. N, 5.58; S, 12.38.

The Imide,  $NO_2.C\overset{4}{H}_3.C\overset{5}{H}_2$    $NH$ .—When the cold mother liquor

from the crystallization of the ammonium salt of the imide is made acid with hydrochloric acid, the imide separates almost quantitatively from the solution. It is colorless, and the crystals as viewed under the microscope are platelike needles. The insolubility of the precipitate makes it unnecessary to purify except by washing with water until free from chlorides. The imide is bitter tasting. It is readily soluble in alkali and forms salts with various metals by which it may be characterized more completely. Its melting point is  $213.5^{\circ}$ .

Calc. for N, 11.57; S, 13.22. Found: N, 11.77, 11.68; S, 13.25.

The *silver* salt of the imide,  $C_8H_5O_6SN_2Ag$ , was obtained by adding a solution of silver nitrate to a hot aqueous solution of the imide. It separates in platelike needles and is less soluble than the silver salt of the cyan-acid to be described later.

Calc. for Ag, 30.92. Found: Ag, 30.87.

The *potassium* salt of the imide was obtained by adding an excess of a concentrated potassium carbonate solution to an aqueous solution of the ammonium salt. It crystallizes in plates, and has a weak bitter taste.

Calc. for K, 13.96. Found: K, 13.91.

**B. From the Unsymmetrical Chloride.**—If the acid chloride melting at  $83^{\circ}$  is treated with cold concentrated ammonia, an action takes place

which, while beginning slowly, at last goes on rapidly with the evolution of heat. The behavior in this respect is characteristically different from that of the symmetrical chloride. In making the ammonia derivative in practice, the ammonia was diluted with three parts of water to lessen the action. If the ammonia is evaporated off and the remaining liquid is concentrated and cooled, crystals form in nodules. These crystals are not as sharply defined as those of the corresponding ammonium salt of the imide; the nodules appear to be made up of compact masses of radiating crystals which branch continually into fanlike shapes. When these nodules are crushed, it is impossible to find any characteristic crystalline form. Recrystallized from alcohol, however, the crystals were not bunched but seemed to be laminated plates almost cubical in form, but with no smooth surfaces. The yield of the product is good. In no case was there any indication of the ammonium salt of the imide. The salt is more soluble than the ammonium salt of the imide. Its melting point is  $310-311^{\circ}$ , with decomposition. It is the ammonium salt of 5-nitro-4-methyl-2-cyanbenzenesulfonic acid. It has a very bitter taste. The free acid was not prepared.

Calc. for  $C_8H_5O_6N_3S$ : N, 16.21; S, 12.35. Found: N, 16.11, 15.95; S, 12.31, 12.24.

The *silver salt*,  $C_8H_5O_6SN_2Ag$ , was prepared by adding a silver nitrate solution to a hot dilute aqueous solution of the ammonium salt. It forms needles and contains no water of crystallization.

Calc. for Ag, 30.92. Found: 30.81.

The *potassium salt*,  $C_8H_5O_6SN_2K$ , made from the ammonium salt and potassium carbonate, separates in plates with no water of crystallization. It has a bitter taste.

Calc. for K, 13.96. Found: 14.03.

### Derivatives Obtained by the Action of Aniline on the Acid Chlorides.

A. **From the Symmetrical Chloride.**—The formation of the anilides of the acid chlorides by previous experimenters in this field has been carried out in three ways: first, by the treatment of the solid acid chloride with aniline; second, by the treatment of the acid chloride with aniline in ether or chloroform solution; and third, by the action of aniline on the acid chloride in the presence of water. The first method has been found to be unsatisfactory. In general, the third method has been chosen by Remsen and his students as it seemed to give the most constant results. In this work, however, it has been found that by using carbon tetrachloride as the solvent the products were of the same nature as those obtained by the aqueous method. The process is shorter and the substances are easily separated from one another.

From the symmetrical acid chloride two products were obtained. One of these, which is insoluble in cold, reasonably dilute sodium hydroxide,

is known as the *anil*. It resembles the imide in many respects, but does not form salts as it contains no imido hydrogen. The other product is the *symmetrical dianilide*.<sup>1</sup>

The Anil,  $\text{NO}_2.\overset{4}{\text{CH}_3}.\overset{5}{\text{C}_6\text{H}_2} \begin{cases} \text{C} = \text{O} \text{ (1)} \\ > \text{N}.\text{C}_6\text{H}_5. \\ \text{SO}_2 \text{ (2)} \end{cases}$ —One gram of the symmet-

rical acid chloride was dissolved in about 50 cc. of carbon tetrachloride at boiling temperature. While this was hot there was added aniline in excess of the amount calculated for the dianilide. This aniline also was dissolved in carbon tetrachloride, and the mixture was warmed for an hour. There was only a slight precipitate at the end of that time, hence the carbon tetrachloride was evaporated and the residue treated with dilute hydrochloric acid. After kneading the residue, which at this stage was oily in nature, for several minutes, the mass solidified. It was then broken up into fine fragments and was allowed to stand overnight in order that the excess aniline might all dissolve as the hydrochloride. The residue was filtered, ground in a mortar with hydrochloric acid, filtered and washed with water to remove the excess of acid. It was next treated with cold, dilute potassium hydroxide. The solution became bright yellow, and a dirty white precipitate was left in an amount small as compared with the bulk of the original precipitate. This insoluble material, which was the anil, was washed with water, dried, and recrystallized from alcohol. The yield of crude anil was 0.27 g.

The anil is very insoluble in alcohol except close to the boiling point. About one hundred cc. of alcohol were required to recrystallize the anil as above. When pure, it is nearly white, and crystallizes in needles which have a melting point of 202–203°.

Calc. for N, 8.81. Found: N, 9.00.

The Symmetrical Anilide,  $\text{NO}_2.\overset{4}{\text{CH}_3}.\overset{5}{\text{C}_6\text{H}_2} \begin{cases} \text{CO.NHC}_6\text{H}_5 \text{ (1)} \\ \text{SO}_2.\text{NHC}_6\text{H}_5 \text{ (2)} \end{cases}$ —The

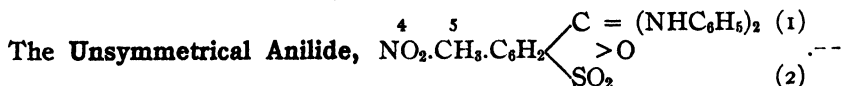
sodium hydroxide solution filtered from the anil was acidified with hydrochloric acid. A white, curdy precipitate at once came down and was filtered off and washed free from acid. It was then redissolved and reprecipitated for further purification. Finally, it was washed, dried, and recrystallized from 75% alcohol. It formed a fine, cottony mass of soft needles with a melting point of 195°. The yield of the anilide was 0.98 g. The substance was identified in this case not by analysis but by its exact correspondence with the dianilide formed under like conditions as a derivative of the unsymmetrical acid chloride. Mixtures of the two preparations showed the same melting point as that of either of the pure specimens.

<sup>1</sup> See Remsen and Kohler, *Am. Chem. J.*, 17, 338 (1895).

List and Stein<sup>1</sup> state that there are three products formed by the action of aniline on<sup>o</sup> the symmetrical chloride, but there was no indication of a third compound here, and a consideration of the yields obtained will show that no very large amount of the material is unaccounted for.

**B. From the Unsymmetrical Chloride.**—The unsymmetrical chloride was dissolved in carbon tetrachloride and to the hot solution was added a carbon tetrachloride solution of aniline so long as a white precipitate continued to form. Hydrochloric acid vapor was evolved copiously, and aniline hydrochloride apparently did not form to any great extent. The precipitate thus formed, on being stirred, gathered into a gummy mass which hardened as the solution cooled. The carbon tetrachloride solution was evaporated to dryness and the whole solid residue ground with hydrochloric acid in a mortar and then allowed to stand to remove soluble products. After some hours it was filtered and washed with a considerable amount of water. The insoluble precipitate was treated with dilute sodium hydroxide in which it was almost completely soluble. Only a faint cloudiness remained in the solution, hence but the merest traces of anil could have been formed. This corresponds with the observation by Holmes<sup>2</sup> that no anil was produced from the unsymmetrical chloride of *o*-sulfo benzoic acid. From this solution the anilide was precipitated by hydrochloric acid, washed, dried and recrystallized from alcohol. It was found, however, that a large portion of the precipitated material would not dissolve in hot alcohol. The insoluble portion proved to be the *unsymmetrical anilide* described later. The portion which dissolved gave needles which melted at 195°, and were the *symmetrical anilide*. It is tasteless, and identical with the anilide formed from the symmetrical acid chloride.

Calc. for N, 10.22; S, 7.78. Found: N, 10.15, 10.06; S, 7.91.



The substance insoluble in alcohol was purified by dissolving in hot 75% alcohol with the aid of sodium hydroxide added drop by drop until the precipitate had disappeared. To this solution acid was added, and the precipitate which formed after a delay of some seconds was nicely crystalline. The crystals were very fine. The melting point seemed to be at 342°; but fusion did not occur until after the product was quite black with heating.

The unsymmetrical anilide is insoluble in most ordinary solvents and this is a general characteristic of such substances. Carbon tetrachloride, alcohol and benzene have little, if any, action on it.

<sup>1</sup> *Loc. cit.*

<sup>2</sup> *Am. Chem. J.*, 30, 275 (1903).

Calc. for N, 10.22; S, 7.78. Found: N, 10.02; S, 7.77, 7.69.

A third substance is produced by the action of aniline on the unsymmetrical chloride. It is soluble in water and may be recovered from the various washings of the original dianilide by evaporation. It crystallizes in needles. It is suspected that this body is the anilido acid, but it is difficult to purify and no satisfactory analyses were obtained of it. While the total yields of the two anilides obtained from the unsymmetrical acid chloride were almost equal in amount, the weight of the third substance is considerably less than either.

#### Transformations of the Aniline Derivatives.

When either the symmetrical or unsymmetrical anilide is treated with phosphorus oxychloride, at boiling temperature, for about one-half hour, a yellow colored solution is produced. If the excess of phosphorus oxychloride is distilled off with care, an air blast being used to help the process, a thick, brownish oil is left, which after being cooled and treated with water to remove phosphoric acid, becomes a bright yellow

powder. This powder is the dianil,  $\text{NO}_2 \cdot \text{CH}_3 \cdot \text{C}_6\text{H}_2$   $\begin{cases} \text{C} = \text{NC}_6\text{H}_5 & (1) \\ > \text{NC}_6\text{H}_5 \\ \text{SO}_2 & (2) \end{cases}$ .

It crystallizes from dilute acetone in short, bright yellow, hexagonal needles. It is soluble in benzene and alcohol, and melts at 188°.

Calc. for N, 10.69; S, 8.14. Found: N, 10.76; S, 8.10.

When the dianil<sup>1</sup> is boiled with concentrated hydrochloric acid it goes over into the colorless anil without dissolving, and the yellow color slowly disappears during the process. The melting point of the colorless solid, 202°, shows it to be the anil.

If the dianil is boiled for some time with glacial acetic acid until the solution, which is vivid yellow at first, becomes colorless, and the solution is allowed to stand, the unsymmetrical anilide crystallizes out. When washed with water and dried it has a melting point of approximately 342°, as described previously.

If the anil is warmed with aniline for some hours, and the excess of aniline distilled off with steam, the residue when recrystallized from alcohol, proves to be the fusible or symmetrical anilide with a melting point of 195°.

#### Derivatives Obtained by the Action of Alcohol on the Acid Chlorides.

In all of the experiments with the alcoholic derivatives of the two acid chlorides, the final products are the same, the only difference being the formation of the ester of the sulfone chloride as an intermediate product in the action of the alcohol on the unsymmetrical acid chloride.\*

<sup>1</sup> See Blanchard, *Am. Chem. J.*, 30, 485 (1903); Henderson, *Ibid.*, 25, 1 (1901).

<sup>2</sup> See Kastle, *Am. Chem. J.*, 11, 181 (1889); Sohon, *Ibid.*, 20, 260 (1898); Henderson, *Ibid.*, 25, 8 (1901); Chambers, *Ibid.*, 30, 387 (1903).



**Methyl Ester Sulfone Chloride**,  $\text{NO}_2\text{.CH}_3\text{.C}_6\text{H}_2\text{.COOCH}_3\text{.SO}_2\text{Cl}$ .—This substance was prepared from the unsymmetrical acid chloride by dissolving in hot methyl alcohol. The warming was kept up only long enough to obtain solution. When the solution was cooled, the sulfone chloride ester separated in long, platelike crystals which were recrystallized from ligroin. It is very soluble in benzene, alcohol, acetone, ether and chloroform. After standing overnight in a desiccator, the product, which has a melting point of  $101^\circ$ , was analyzed.

Calc. for N, 4.77; S, 10.92; Cl, 12.08.

Found: N, 4.66, 4.61; S, 10.75, 11.02; Cl, 12.09, 12.01.

The *ethyl ester sulfone chloride* was also prepared and analyzed. It melts at  $72^\circ$ .

**Methyl Benzoic Ester of the Sulfonic Acid**,  $\text{NO}_2\text{.CH}_3\text{.C}_6\text{H}_2\text{.COOCH}_3\text{.SO}_2\text{OH}$ .—The methyl ester acid was prepared by boiling either acid chloride with methyl alcohol for some time and evaporating to a syrup. On cooling, it slowly formed crystals which, on account of their extreme solubility, were not purified. The identification was by means of the barium salt, which could be made easily. The silver salt, which was very soluble, was made but not analyzed. It was used in the preparation of the dimethyl ester. The barium salt contains no water of crystallization, and gave the following result upon analysis:

Calc. for Ba, 20.04. Found: Ba, 20.05.

The *ethyl benzoic ester* was also prepared.

**The Dimethyl Ester**,  $\text{NO}_2\text{.CH}_3\text{.C}_6\text{H}_2\text{.COOCH}_3\text{.SO}_2\text{OCH}_3$ .—The dimethyl ester cannot be made by the direct action of the acid chlorides on alcohol. Neither does the action of sodium methylate,<sup>1</sup> either dry or in absolute alcohol, upon an absolute ether solution of the acid chloride prove of much value. The best method was that of treating the silver salt of the methyl ester acid with methyl iodide in a pressure bottle as recommended by Kastle.<sup>2</sup> After heating the mixture some time at  $100^\circ$  the excess of methyl iodide is evaporated off and the residue extracted with absolute ether. The product obtained by evaporating the ether and recrystallizing from absolute methyl alcohol melted at  $94.5^\circ$ . It is insoluble in water, has a neutral reaction, and contains no halogen.

Calc. for N, 4.85. Found: N, 4.98.

#### Derivatives Obtained by the Action of Phenol on the Acid Chlorides.

The action of phenol upon the acid chlorides is of the same general nature as that given by the alcohols. Both acid chlorides seem to give

<sup>1</sup> Cobb, *Am. Chem. J.*, 35, 488 (1908).

<sup>2</sup> *Loc. cit.*

practically the same derivatives,<sup>1</sup> the relative amounts of which depend upon the temperature. At the same time there is usually formed a water-soluble red substance, probably a phthalein, which has not been investigated.

The **Diphenyl Ester**,  $\text{NO}_2\text{CH}_3\text{C}_6\text{H}_2\text{COOC}_6\text{H}_5\text{SO}_2\text{OC}_6\text{H}_5$ .—Three methods were used in preparing the diphenyl ester. First, the acid chloride was warmed with phenol. The production of phthalein was so marked that this method was used only for a trial preparation. The di-ester appears to be the only product outside of the phthalein.

Second, the Schotten-Baumann method was tried. The acid chloride was dissolved by gentle warming in a slight excess of phenol and dilute potassium hydroxide solution. The yellow oil which first formed soon solidified and was recrystallized from organic solvents. The amount of phthalein formed was small.

The third method consisted of treating the acid chloride with a mixture of pyridine and phenol. Two grams of phenol and an equal amount of pyridine were mixed in a small beaker and the powdered acid chloride added.

When the acid chloride had dissolved in the pyridine phenol solution the liquid was allowed to stand at room temperature for the completion of the reaction. Alcohol was then added and warmed until all the compound was in solution. As the liquid cooled, crystals formed as colorless, flat needles somewhat resembling those of the ethyl benzoic ester of the sulfone chloride. These contained no chlorine, however, and were the diphenyl ester. The melting point of the crude product is, according to our experience, always  $115^\circ$  or  $116^\circ$ , but by recrystallization from alcohol, benzene, alcohol, glacial acetic acid, and alcohol in the order named, the melting point becomes constant at  $123^\circ$ . The products which were obtained separately from the symmetrical and unsymmetrical acid chlorides are identical in this respect as in all others. No sulfone chloride was formed by any of these three methods, a fact which was due in all probability to the temperature employed.

Calc. for N, 3.39; S, 7.75. Found: N, 3.42, 3.47; S, 7.74, 7.86.

### Summary.

1. Two acid chlorides, the symmetrical with a melting point of  $134^\circ$ , the unsymmetrical with a melting point of  $83^\circ$ , have been prepared. These compounds were peculiar only in that they could be separated by fractional crystallization from solution, and that when pure, they did not tend in the least to form constant melting-point mixtures. Two crystalline forms of the symmetrical acid chloride were isolated, but their differences were not investigated closely.

<sup>1</sup>Humphreys, *Am. Chem. J.*, 30, 292 (1903); Chambers, *Ibid.*, 30, 374 (1903).

2. The derivative obtained by the action of ammonia upon the symmetrical acid chloride was the ammonium salt of the imide. From this the imide itself was prepared by the action of dilute hydrochloric acid. The silver salt and the potassium salt of the imide also were made and analyzed.

3. The derivative obtained by the action of ammonia on the unsymmetrical acid chloride was the ammonium salt of the cyan acid; no imide was found. The silver and potassium salts of the cyan acid also were made and analyzed.

4. The derivatives obtained by the action of aniline on the symmetrical acid chloride were the symmetrical dianilide and the anil.

5. The derivatives obtained by the action of aniline on the unsymmetrical acid chloride were the symmetrical dianilide and the unsymmetrical dianilide.

6. By the action of phosphorus oxychloride, each of the two dianilides was transformed into the dianil. This in turn when heated with concentrated hydrochloric acid gave the anil or, heated with glacial acetic acid it gave the unsymmetrical dianilide.

7. The derivative obtained by the action of the alcohols on the symmetrical acid chloride was the benzoic ester of the sulfonic acid.

8. The derivatives obtained by the action of alcohols on the unsymmetrical acid chloride were the benzoic ester of the sulfone chloride, and the benzoic ester of the sulfonic acid.

9. The derivative obtained by the action of phenol upon either of the acid chlorides was always the diphenyl ester. No particular effort was made to prepare the phenyl sulfone chloride. When pyridine was used in the reaction, a second substance was formed which may be the pyridine salt of the phenyl benzoic ester acid. Its constitution was not established.

10. By the action of methyl iodide on the silver salt of the methyl benzoic ester acid, the dimethyl ester was formed.

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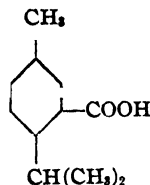
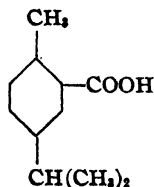
[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY.]  
**THE SYNTHESIS OF *p*-CYMENE 2-MONOCARBOXYLIC ACID  
 AND OF *p*-CYMENE 3-MONOCARBOXYLIC ACID, TO-  
 GETHER WITH CERTAIN OF THEIR DERIVATIVES.**

BY MARSTON TAYLOR BOGERT AND JOHN ROSS TUTTLE.<sup>1</sup>

Received May 12, 1916.

The acids which are the subject of the present article are depicted by the following structural formulas:

<sup>1</sup> The experimental work upon which this paper is based was carried out by Mr. Tuttle in partial fulfilment of the requirements for the degree of Doctor of Philosophy under the Faculty of Pure Science of Columbia University.



***p*-Cymene 2-Monocarboxylic Acid. *p*-Cymene 3-Monocarboxylic Acid.**

**I. *p*-Cymene 2-Monocarboxylic Acid.**—Paterno and Fileti,<sup>1</sup> in 1875, fused cymene sodium sulfonate with potassium cyanide and saponified the dark colored crude product with alcoholic potassium hydroxide solution, obtaining what was apparently the amide (m. 138–9°, corr.) of the cymene 2-carboxylic acid.

Four years later, Paterno and Spica,<sup>2</sup> by hydrolysis of this amide, secured what they believed to be the cymene carboxylic acid itself as a solid crystallizing from water in fine needles, m. 63°, but failed to get enough pure material for an analysis. They also endeavored to prepare this acid by the fusion of the corresponding cymene sodium sulfonate with sodium formate, and by the action of CO<sub>2</sub> and metallic sodium upon bromocymene, but were unsuccessful in both cases.

Kreysler<sup>3</sup> heated tricarvacryl phosphate with potassium cyanide and obtained, in an impure form, the nitrile of the desired acid. By heating this nitrile with alcoholic potassium hydroxide solution under pressure and purifying the product, an acid was isolated which on analysis gave figures agreeing with those calculated for cymene carboxylic acid. He described his product as forming colorless needles, m. 75°, and also prepared a silver salt.

In 1886, Cropp<sup>4</sup> described as a cymene monocarboxylic acid a substance m. 272° resulting from the oxidation of methyl *p*-cymyl ketone. Murtfeld,<sup>5</sup> in the following year, obtained an acid, m. 272°, by oxidation of di-*p*-cymyl ethylene diketone with dilute nitric acid at 150°, which he regarded as a cymene monocarboxylic acid and as probably identical with the acid mentioned by Cropp. Claus,<sup>6</sup> however, later showed that the supposititious cymene carboxylic acid of Cropp and Murtfeld was in all probability a mixture consisting mainly of methyl isophthalic acid (m. 320–330°).

Claus,<sup>7</sup> and Neukranz<sup>8</sup> by careful oxidation of methyl *p*-cymyl ketone

<sup>1</sup> *Gazz. chim. ital.*, 5, 30 (1875).

<sup>2</sup> *Ibid.*, 9, 400 (1879).

<sup>3</sup> *Ber.*, 18, 1714 (1885).

<sup>4</sup> *Inaug. Diss.*, Freiburg, 1886; *Ber.*, 19, 233 (1886).

<sup>5</sup> *Inaug. Diss.*, Freiburg, 1887.

<sup>6</sup> *J. prakt. Chem.*, [2] 43, 138 (1891).

<sup>7</sup> *Loc. cit.*

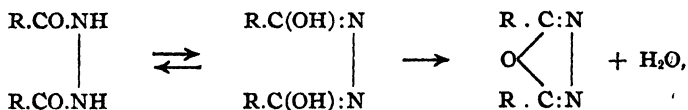
<sup>8</sup> *Inaug. Diss.*, Freiburg, 1891.

with potassium permanganate, obtained a small amount of the cymene 2-carboxylic acid in small, colorless needles, m.  $69^{\circ}$  (uncorr.), which they stated sublimed in crystals when heated. In addition to the free acid, Neukranz prepared also the K, Ba, Ca, Cu and Ag salts, as well as an impure sodium salt. So far as we have been able to discover, these salts have never been described in any of the chemical journals and appear only in the above dissertation.

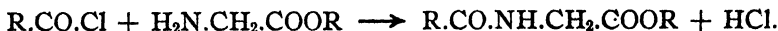
To sum up: small amounts of the free acid have been obtained hitherto and its m. p. has been given by these investigators as  $63^{\circ}$ ,  $69^{\circ}$  or  $75^{\circ}$ ; K, Ba, Ca, Cu, Ag and an impure Na salt have been described; also an amide and an impure nitrile.

The original work reported in the Experimental Part includes a method for preparing this acid in any desired amount from 2-bromocymene by the Barbier-Grignard reaction, a study of various salts and of the amide, the preparation and characterization of the hitherto unknown methyl and ethyl esters, the acid chloride, anilide, diacyl hydrazine,  $\alpha, \alpha'$ -dicymyl-[*bb*]-furodiazole, 2-methyl-5-isopropylhippuric acid and its ethyl ester. Preliminary studies have also been made upon the bromination of the free acid.

The furodiazole was easily obtained by the dehydration of the di-acyl hydrazine, as follows:



and the hippuric acid derivative by condensing the acid chloride with glycine ester,



Incidentally, the experiments showed that the bromocymene produced by direct bromination of the hydrocarbon is not, as has been supposed hitherto, pure 2-bromocymene; but generally contains some of the 3-bromo isomer also, which cannot be separated by any ordinary fractional distillation.

The process of Paterno and Fileti, and of Paterno and Spica, has been repeated, and it has been found that the acid so obtained was an impure cymene 2-monocarboxylic acid.

**II. *p*-Cymene 3-Monocarboxylic Acid.**—Our search of the literature has so far failed to disclose any record of this acid or of any of its derivatives. The only reference to attempts to prepare it, appears to be the statement of Kreysler<sup>1</sup> that he endeavored unsuccessfully to obtain it by distilling tri-thymyl phosphate with potassium cyanide and saponi-

<sup>1</sup> *Loc. cit.*

fying the product; but he failed to get either the pure nitrile or sufficient of the acid to analyze or identify.

In the Experimental Part is recorded the synthesis of this acid from 3-bromocymene by the Barbier-Grignard reaction; also the preparation of its Na, K, Ba, Ca, Cu and Ag salts; its methyl, ethyl and phenyl esters, acid chloride, amide, anilide, and diacyl hydrazine; and, from the latter, the  $\alpha, \alpha'$ -dicymyl- $[bb_1]$ -furodiazole and N-phenyl- $\alpha, \alpha'$ -dicymyl- $[bb_1]$ -pyrroldiazole; and the 3-methyl-6-isopropylhippuric acid from the acid chloride and glycine.

The yield of both cymene carboxylic acids was greatly increased by employing  $\text{CO}_2$  under pressure, and a "Prana" carbonating siphon proved most convenient for the purpose.

#### EXPERIMENTAL PART.

##### I. *p*-Cymene 2-Monocarboxylic Acid.

**Cymene.**—The cymene used in these experiments was purified by the following process: (1) fractional distillation at ordinary pressure, (2) digestion with metallic sodium or phosphoric anhydride, (3) fractional distillation under reduced pressure, and (4) finally repeated rectification over metallic sodium at ordinary pressure. In spite of this, we failed to get a constant and unvarying boiling point, the purified hydrocarbon generally showing a corrected b. p. varying between the limits  $176.5^\circ$  and  $178^\circ$  at ordinary pressure. Density and refractive index determined on different lots showed the following range:  $D_{15} \ 0.8615$  to  $0.8622$ ;  $N_D^{20} \ 1.4883$  to  $1.4897$ . This refractive index agrees with that calculated for the sodium line from the figures given by Perkin<sup>1</sup> for pure cymene at  $4^\circ$ , namely  $\mu \ 7.9^\circ/4^\circ = 1.49664$ . Assuming that the difference for  $1^\circ$  is approximately that for benzene, namely  $0.00066$ , then  $N$  at  $20^\circ$  would be  $1.49664 - 0.00799 = 1.48865$ . Examined in a 200 mm. tube, the hydrocarbon showed no trace of rotation.

*2-Bromocymene* has been prepared by the direct bromination of cymene, in presence of small amounts of iodine as catalyst, by Landolph,<sup>2</sup> Fittica,<sup>3</sup> and by Remsen and Day;<sup>4</sup> by Kelbe and Koschnitzky,<sup>5</sup> by warming cymene sulfo acid with bromine water; and by Klages and Kraith<sup>6</sup> by the action of  $\text{PBr}_5$  upon carvone. The b. p. is variously stated by these investigators as  $228-9^\circ$  (Fittica),  $233^\circ$  (Klages and Kraith)  $233-5^\circ$ , (in vapor) (Landolph), and  $237^\circ$  (corr.) (or  $228-9^\circ$ , uncorr.) (Remsen and Day).

According to our experiments, the most convenient method of prepara-

<sup>1</sup> *J. Chem. Soc.*, 77, 279 (1900).

<sup>2</sup> *Ber.*, 5, 267 (1872).

<sup>3</sup> *Ann.*, 172, 311 (1874).

<sup>4</sup> *Am. Chem. J.*, 5, 150 (1883).

<sup>5</sup> *Ber.*, 19, 1732 (1886).

<sup>6</sup> *Ibid.*, 32, 2557 (1899).

tion proved to be the following: Bromine (about 10% excess) was added very gradually to pure cymene containing a small amount of iron powder as catalyst, the reaction being carried out in a flask protected from strong daylight, and cooling when necessary to moderate the reaction. The mixture was then warmed on the water bath, the HBr and excess of bromine blown out by a current of dry air, the crude product washed with water, digested with warm sodium carbonate solution, washed again with water, distilled with steam, the oily layer separated from the distillate, dried over calcium chloride, and fractioned under reduced pressure. The fraction b. 116.5–118.5° at 14.7 mm. (corr.) was employed in the subsequent experimental work. The yield of this purified material from 915 g. cymene amounted to 630 g. and its uncorrected b. p. at ordinary pressure was 231–3°.

The use of an excess of bromine was found to increase the yield of bromocymene, whereas the length of time the reaction mixture was allowed to stand after the addition of the bromine did not appear to influence the yield materially. Iron powder proved a much more active catalyst than iodine for this reaction. Fractionation under diminished pressure was necessary, as some decomposition occurred at the ordinary pressure. No unchanged cymene was found in the product, and the purified substance was colorless with a pleasant odor somewhat recalling that of cymene itself. The subsequent work with this product, however, proved conclusively that it was contaminated with the 3-bromo isomer, and the boiling points of the two lie so close together that it was impossible to separate them by fractional distillation.

Some 2-bromocymene was, therefore, prepared also by the action of PBr<sub>3</sub> upon purified carvacrol, in practically the same way as Fileti and Crosa<sup>1</sup> made the 3-bromo isomer from thymol. The yield was not very good, as considerable of the phenol remains behind as a phosphoric ester (from which it can be recovered if desired). 57 g. carvacrol gave 8.6 g. of the 2-bromocymene, b. 232–5° (uncorr.).

Large amounts of bromocymene can be prepared easily by the direct bromination of the hydrocarbon, as described above, but the product is a mixture of the two isomers. On the other hand, it is not very convenient to prepare large amounts of 2-bromocymene from carvacrol, but the product so obtained is free from the 3-bromo isomer.

**Cymene 2-Carboxylic Acid.**—In view of Landolph's observation<sup>2</sup> that the bromine in 2-bromocymene does not react with metallic sodium, alone or in the presence of methyl iodide or CO<sub>2</sub>, it was to be expected that it would prove somewhat unreactive even with magnesium, and this was found to be the case not only with this particular bromocymene

<sup>1</sup> *Gazz. chim. ital.*, 16, 292 (1886).

<sup>2</sup> *Loc. cit.*

but also with the isomeric 3-bromo compound. An anhydrous ethereal solution of either compound showed no evidence of any reaction upon boiling with metallic magnesium for about an hour, even after the addition of small amounts of iodine. To activate the magnesium, it was found advantageous to add a few drops of ethyl iodide. If, then, after a few minutes' standing, the anhydrous ether solution of bromocymene was added, the mixture being warmed, the reaction began immediately and proceeded to completion without further external heating, the bromocymene solution being added gradually from time to time. When the latter had all been added, the solution was heated for a short time on the water bath, when the magnesium almost wholly dissolved. The solution was cooled, and siphoned carefully into a "Prana" carbonating flask in such a way as to avoid contact with the moisture of the air, both containers being protected by calcium chloride guard tubes. The Prana flask was kept in a freezing mixture, and the solution therein treated with  $\text{CO}_2$  under pressure for several hours, using capsules of the liquid gas. This caused the mixture to separate into a clear upper ethereal layer and a lower darker one. The contents of the flask were decomposed with ice and dilute hydrochloric acid in the usual way, extracted with ether, the ether solution extracted in turn with sodium carbonate or potassium hydroxide solution, the alkaline solution concentrated somewhat, acidified with dilute hydrochloric acid, the white precipitate filtered out, washed, dried, and recrystallized. The yield of pure acid amounted to about 35%, when a pure 2-bromocymene was used. If the  $\text{CO}_2$  was not used under pressure, the yield was much less.

The 2-bromocymene used in the early experiments was made from carvacrol, so as to avoid complications due to the presence of the isomer. In a sample experiment, 8.6 g. of the bromocymene and 1 g. magnesium, yielded 2.7 g. of the crude acid, or about 40% of the theoretical. A small amount of cymene was usually formed in the reaction.

The crude acid was purified by dissolving it in about its own weight of glacial acetic acid, adding water until the solution clouded, warming until it cleared, and then allowing the solution to cool slowly, finally in the ice box. It can be crystallized also from dilute alcohol, but the crystals are not usually so fine as those secured by the above method.

The pure acid forms large, colorless, brittle, glassy prisms, m.  $71.7^\circ$  (corr.), difficultly soluble in cold water, slightly in hot; soluble in methyl or ethyl alcohol, ether, ligroin, benzene, xylene, chloroform, carbon tetrachloride, acetone, carbon disulfide, glacial acetic acid or ethyl acetate. It volatilizes slowly with steam, but does not sublime, contrary to the statement of Claus and Neukranz.<sup>1</sup> It can be distilled under reduced

<sup>1</sup> *Loc. cit.*



pressure, and boils at about  $171-2^{\circ}$  at 20 mm. Distilled with excess of soda lime,<sup>1</sup> it gives cymene again.

The following analysis was made of a sample of purified acid prepared from cymene:

Subs. 0.1662:  $\text{CO}_2$ , 0.4515;  $\text{H}_2\text{O}$ , 0.1137. Calc. for  $\text{C}_{11}\text{H}_{14}\text{O}_2$ : C, 74.16; H, 7.87. Found: C, 74.09; H, 7.60.

Cryoscopic molecular weight determinations in acetic acid gave the figures 171 and 176, while the calculated molecular weight is 178.

The preparation of pure 2-acid from the bromocymene obtained from cymene proved very troublesome, on account of the presence of the 3-isomer. In one experiment, for example, a mixture of 200 g. bromocymene, 23 g. magnesium and 400 cc. anhydrous ether, was treated for about  $10\frac{1}{2}$  hours with  $\text{CO}_2$  under pressure, supplying the latter as fast as it was absorbed. In all, a total of 68 g. liquid  $\text{CO}_2$  was used, the amount theoretically required being about 40 g. The reaction was conducted at a temperature of  $-13^{\circ}$  to  $-3^{\circ}$ . 60 g. of crude acid were obtained, as a yellowish semi-solid mass, which proved very difficult to purify. By fractional crystallization, only 30 g. of pure 2-acid could be recovered. The mother-liquors were united, the acid neutralized with sodium carbonate, the solution filtered, washed with ether, warmed to eliminate any dissolved ether, and then fractionally precipitated with dilute hydrochloric acid. The 2-acid was found in the first fractions, the 3-acid in the later ones, the intermediate fractions being mixtures of the two.

In another experiment, 230 g. bromocymene and 27 g. magnesium were used, and the crude acid was distilled under reduced pressure. 105 g. of impure 2-acid resulted, from which by filtering and pressing 79 g. solid acid were obtained. When these 79 g. were converted into the sodium salt and the solution of the latter precipitated fractionally by dilute hydrochloric acid, 36 g. pure 2-acid and 9 g. pure 3-acid were recovered.

**Sodium Salt, NaA.**—This was prepared in the same way as described below for the potassium salt. It does not crystallize well, but forms a white powder, without water of crystallization, and is not hygroscopic.

Subs. 0.3190:  $\text{Na}_2\text{SO}_4$ , 0.1105. Calc. for  $\text{C}_{11}\text{H}_{13}\text{O}_2\text{Na}$ : Na, 11.50. Found: Na, 11.23.

Neukranz<sup>1</sup> prepared a sodium salt, which on analysis was found to contain 23.22% sodium, and which must, therefore, have been very impure. Apparently, his calculations misled him, as he puts down for the calculated percentage of sodium in this salt 23.5, whereas as a matter of fact it is 11.5, as stated above.

**Potassium Salt, KA.H<sub>2</sub>O.**—A 5% aqueous solution of potassium hydroxide was treated with a slight excess of the 2-acid, the mixture allowed to stand for a few hours and the excess of free acid (which is prac-

<sup>1</sup> *Loc. cit.*

tically insoluble in cold water) then filtered off. The filtrate was concentrated on the water bath to a paste and then placed in a desiccator where it gradually became crystalline. It carries one molecule of water of crystallization, but is not appreciably hygroscopic.

0.2550 g. salt dried to constant weight in desiccator over  $\text{H}_2\text{SO}_4$ , and then heated to constant weight at  $115^\circ$ , lost 0.0194 g. Calc. for  $\text{C}_{11}\text{H}_{13}\text{O}_2\text{K}\cdot\text{H}_2\text{O}$ :  $\text{H}_2\text{O}$ , 7.69. Found:  $\text{H}_2\text{O}$ , 7.61.

Anhydrous salt, 0.2845:  $\text{K}_2\text{SO}_4$ , 0.1142. Calc. for  $\text{C}_{11}\text{H}_{13}\text{O}_2\text{K}$ : K, 18.09. Found: K, 18.03.

It forms small, colorless, glassy crystals. Neukranz makes no mention of any water of crystallization in the potassium salt he prepared.

**Calcium Salt,  $\text{CaA}_2\cdot 2\text{H}_2\text{O}$ .**—This was made in the same manner as the barium salt below. In water, it is much less soluble than the latter, and but little more soluble in hot water than in cold. Upon evaporation of the aqueous solution, the salt separates gradually in fine colorless crystals, which were dried in a desiccator.

Heated to const. wt. at  $105\text{--}10^\circ$ , the salt lost 8.32%. Calc. for  $2\text{H}_2\text{O}$ : 8.37%.

Anhydrous salt, 0.2765:  $\text{CaSO}_4$ , 0.0952. Calc. for  $(\text{C}_{11}\text{H}_{13}\text{O}_2)_2\text{Ca}$ : Ca, 10.15. Found: Ca, 10.12.

Neukranz also reports the calcium salt as containing two molecules of water of crystallization.

**Barium Salt,  $\text{BaA}_2$ .**—The acid was suspended in water and digested with excess of  $\text{BaCO}_3$  at  $100^\circ$  for three or four hours. It was then filtered, the filtrate again digested with  $\text{BaCO}_3$ , to make sure that all acid was converted into the salt, and once more filtered. The filtrate was concentrated until the salt began to separate and was then left in a desiccator over  $\text{H}_2\text{SO}_4$  for several days, where it slowly solidified. Dried at  $105\text{--}110^\circ$ , and then for two hours at  $120\text{--}5^\circ$ , it lost 1.5% in weight, whereas the loss calculated for one molecule water is 3.42. Evidently the salt either crystallizes without water of crystallization, or else this water is lost partly when the salt is left for a few days over  $\text{H}_2\text{SO}_4$ .

Anhydrous salt, 0.3584:  $\text{BaSO}_4$ , 0.1687. Calc. for  $(\text{C}_{11}\text{H}_{13}\text{O}_2)_2\text{Ba}$ : Ba, 27.90. Found: Ba, 27.70.

The barium salt isolated by Neukranz carried two molecules of water.

The **Copper Salt,  $\text{CuA}_2$** , was prepared by warming a solution of the calcium salt with an excess of copper acetate solution. A voluminous blue precipitate resulted. It was filtered out, washed and dried over  $\text{H}_2\text{SO}_4$ . As no loss of weight occurred at  $120^\circ$ , the salt carries no water of crystallization.

Calc. for  $(\text{C}_{11}\text{H}_{13}\text{O}_2)_2\text{Cu}$ : Cu, 15.23. Found: Cu, 15.62.

This high figure for the copper is probably due to the presence of a little adsorbed copper acetate, as the voluminous precipitate was not easily washed.

Neukranz reports a copper salt carrying one molecule of water of crystallization.

The **Silver Salt**, AgA, was prepared by dissolving the acid in ammonium hydroxide solution, warming to remove all excess of ammonia, and then adding silver nitrate solution. The acid used was obtained from carvacrol, and the salt was, therefore, analyzed completely, as a check upon the accuracy of the work.

Subs. 0.2155, 0.2350: Ag, 0.0814; CO<sub>2</sub>, 0.4012; H<sub>2</sub>O, 0.0946.

Calc. for C<sub>11</sub>H<sub>13</sub>O<sub>2</sub>Ag: Ag, 37.87; C, 46.33; H, 4.56. Found: Ag, 37.77; C, 46.52; H, 4.47.

It is a colorless, crystalline powder, which darkens on standing in the light, and has been prepared also by Kreyser<sup>1</sup> and by Neukranz.

**Methyl Ester**, C<sub>10</sub>H<sub>13</sub>COOCH<sub>3</sub>.—Three grams of methyl alcohol were dissolved in 25 cc. pyridine and 9.5 g. of the chloride of cymene 2-carboxylic acid added gradually with cooling and shaking. The reaction liberated considerable heat, but no precipitate separated until the last few drops of the acid chloride were being run in, when it began to form rapidly and in large amount. After standing for five hours, the mixture was poured into well cooled dilute sulfuric acid. A colorless oil separated, which was removed, washed four times with acidulated water to eliminate all pyridine, then with dilute potassium hydroxide solution to remove any free 2-acid (of which there proved to be very little), after which it was collected with ether, the ethereal solution washed, dried, the ether distilled off and the residue fractioned at a pressure of 16.2 mm. (corr.), the ester coming over at 132°, as a colorless oil of pleasant odor.

Subs. 0.1150: CO<sub>2</sub>, 0.3157; H<sub>2</sub>O, 0.0860. Calc. for C<sub>12</sub>H<sub>16</sub>O<sub>2</sub>: C, 75.00; H, 8.33. Found: C, 74.87; H, 8.31.

The **Ethyl Ester** was obtained by dissolving the acid in a slight excess of potassium hydroxide solution, and then digesting with diethyl sulfate, essentially as described beyond for the ethyl ester of the 3-acid.

It is a colorless heavy oil of pleasant ethereal odor, which can be saponified readily to the acid by alcoholic potassium hydroxide solution.

**Acid Chloride**, C<sub>10</sub>H<sub>13</sub>.CO.Cl.—The anhydrous acid was treated, in a flask provided with a calcium chloride guard tube, with slightly more than the calculated amount of PCl<sub>5</sub>. Upon shaking the mixture, the reaction began almost immediately and proceeded so vigorously that within two or three minutes, with the exception of a small amount of PCl<sub>5</sub>, the whole mass was liquid and quiescent. After standing for three-quarters of an hour, it was warmed for 15 minutes at 100°, when the small amount of undissolved PCl<sub>5</sub> went into solution, and was then transferred to a distilling flask and fractioned under reduced pressure, the acid chloride coming over as a clear colorless liquid of pungent odor, b. 131.5–132°

<sup>1</sup> *Loc. cit.*

at 17.7 mm., or 135.5–136° at 21.5 mm. The yield was usually better than 90%. In one experiment, for example, 21 g. acid gave 23.5 g. of the chloride.

**Acid Amide,  $C_{10}H_{13}.CO.NH_2$ .**—Prepared from the acid chloride, in practically the same way as described beyond for the amide of the 3-acid, this substance crystallizes from ligroin, water or dilute alcohol, in microscopic needles which felt together like shredded asbestos, and m. 147° (corr.). It is soluble in methyl alcohol, ethyl alcohol, or warm benzene; slightly soluble in ether or in cold carbon tetrachloride; insoluble in cold, slightly soluble in hot ligroin. Yield, 95%.

Subs. 0.1878: 12.7 cc. N at 21° and 762 mm. Calc. for  $C_{11}H_{15}ON$ : N, 7.91. Found: N, 7.69.

An attempt to convert this amide into the phenyl hydrazide by heating it for 2½ hours at 150–160° with phenyl hydrazine failed, the amide being recovered practically unchanged.

**Acid Anilide,  $C_{10}H_{13}.CO.NHC_6H_5$ .**—This was obtained from the acid chloride and aniline, in anhydrous ether solution, as outlined beyond for the anilide of the 3-acid. Yield, 87%.

The pure substance crystallizes from ligroin or dilute alcohol in small, colorless, glassy prisms, m. 143.5° (corr.); soluble in methyl or ethyl alcohols, in benzene, chloroform, acetone or amyl acetate; but slightly soluble in ether, hot water or cold ligroin; fairly soluble in cold carbon disulfide or carbon tetrachloride, easily soluble in the same hot.

Subs. 0.2521: 12.4 cc. N at 21° and 756 mm. Calc. for  $C_{17}H_{19}ON$ : N, 5.53. Found: N, 5.54.

**Sym.-2,2'-Dimethyl-5,5'-diisopropyl Dibenzoylhydrazine,  $C_{10}H_{13}.CO.NH.NH.CO.C_{10}H_{13}$ .**—In the production of this diacyl hydrazine, both the ordinary 50% aqueous solution of hydrazine hydrate was employed and also the more concentrated solution obtained by distilling the former until the temperature of the distillate reached 115°, when the residue is stated<sup>1</sup> to contain 55–60% of absolute  $N_2H_4$  or 90% of  $N_2H_4.H_2O$ . The results secured with the 50% aqueous solution were just as good as those with the more concentrated solution.

In a typical experiment, 13.5 g. acid chloride were dissolved in 4 cc. absolute ether and the solution added very gradually with shaking to an excess (approximately 4 mols) of well cooled hydrazine hydrate solution. A white precipitate began to separate immediately and slowly increased in amount. After all the acid chloride had been added (about an hour), the mixture was a white, pasty mass of strong alkaline reaction, due to the excess of hydrazine hydrate present. After standing for three hours, it was filtered, the precipitate washed thoroughly with cold

<sup>1</sup> Curtius, *J. prakt. Chem.*, [2] 42, 523 (1890).

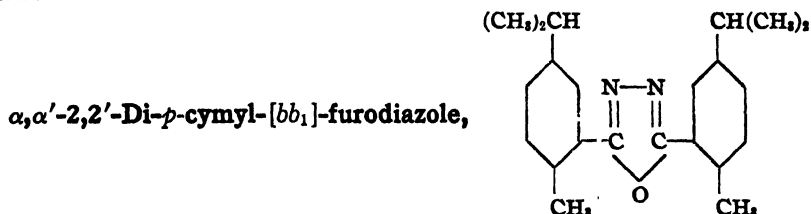
water, dried, and crystallized from dilute alcohol.<sup>1</sup> Yield, 91% (11 g.).

The pure substance crystallizes in minute, colorless, glassy prisms, m. 192° (corr.); insoluble in ligroin or water; moderately soluble in chloroform or acetic acid; little soluble in ether or in cold alcohol, benzene or acetone, but readily soluble in the latter at their b. p. It forms no salts with hydrochloric or nitric acids, even in non-aqueous solvents.

Subs. 0.2341 g.: 16.8 cc. N at 21° and 754 mm. Calc. for  $C_{10}H_{12}.CO.NH.NH.CO.C_{10}H_{12}$ : N, 7.95; for  $C_{10}H_{12}.CO.NH.NH_2$ : N, 14.56. Found: N, 8.07.

An attempt was made to secure the monacyl hydrazine by heating the amide with excess of hydrazine hydrate alone, and in alcoholic solution, but the amide was recovered unchanged in both cases.

The diacyl hydrazine is unattacked by nitrous acid in glacial acetic acid solution.



The diacyl hydrazine was heated for an hour and three-quarters at 260–80° (thermometer in melt), and then cooled. The cold melt was purified by repeated crystallization from methyl alcohol in presence of boneblack.

The pure compound forms small, colorless, glassy prisms, m. 111.5° (corr.), quite soluble in benzene or chloroform, less so in benzine or acetone; slightly soluble in cold methyl alcohol or ethyl alcohol; and practically insoluble in water.

Subs. 0.1579: 11.83 cc. N at 21° and 752 mm. Calc. for  $C_{22}H_{28}ON_2$ : N, 8.38. Found: N, 8.40.

An effort was made to get the corresponding thiodiazole by the action of  $P_2S_5$  upon the diacyl hydrazine, but the product was a mixture of furo- and thiodiazole, from which we failed to isolate any really pure thiodiazole.<sup>2</sup>

**2-Methyl-5-isopropyl Hippuric Acid and its Ethyl Ester,  $C_{10}H_{12}.CO.NH.CH_2.COOH$ .**—35 g. of the acid chloride were added slowly, with cooling and shaking, to an excess of glycine ester in ethereal solution. A white precipitate separated. After standing at laboratory temperature for three hours, the white precipitate of glycine ester hydrochloride was filtered out, and the ethereal filtrate evaporated, leaving an oily residue,

<sup>1</sup> Compare also Pellizzari, *Atti r. Accad. Lincei Roma* [5] 8, I, 327; *Chem. Zentralbl.*, 1899, I, 1240; Stollé, *J. prakt. Chem.*, [2] 69, 474 (1904).

<sup>2</sup> Compare also Stollé, *J. prakt. Chem.*, [2] 69, 157, 374 (1904); Stevens, *Inaug. Diss.*, Heidelberg, 1899.

which was washed with dilute hydrochloric acid to remove any glycine ester present, taken up again with ether, the ethereal solution washed with dilute potassium hydroxide solution, to remove any free 2-acid, then with water, dried with calcium chloride, and the ether removed by evaporation. The residue was an oil, which did not solidify in an ordinary freezing mixture of ice and salt. As it was deemed unwise to attempt further purification by distillation, on account of the small amount in hand and the likelihood of some decomposition on heating,<sup>1</sup> the ester was saponified to the free acid by careful hydrolysis with alcoholic potassium hydroxide solution.<sup>2</sup>

After warming the ester on the water bath for a few minutes, a drop of the mixture was completely soluble in water, showing the total hydrolysis of the ester, and the solution was then largely diluted with water and acidified cold with dilute hydrochloric acid. A yellowish precipitate appeared, which was filtered out, washed, dried, washed with ligroin, to eliminate any 2-acid, again dried, and finally crystallized from very dilute alcohol.

As thus purified, it forms colorless, glassy scales, m.  $183^{\circ}$  (corr.); apparently insoluble in water or ligroin; slightly soluble in benzene, ether or chloroform; quite soluble in methyl or ethyl alcohol or in acetone.

Subs. 0.2632 g.: 14.0 cc. N at  $21^{\circ}$  and 748 mm. Calc. for  $C_{10}H_{12}.CO.NH.CH_2.COOH$ : N, 5.96. Found: N, 5.93.

**Repetition of the Method of Paterno and Fileti,<sup>3</sup> and of Paterno and Spica.<sup>4</sup>**—The anhydrous barium sulfonate of cymene was distilled dry with potassium cyanide, and the sodium sulfonate with potassium cyanide and with potassium ferrocyanide. In all cases, the results were most unsatisfactory, on account of the large amount of decomposition. The best results were secured by intimately mixing 10 g. anhydrous sodium sulfonate with an equal weight of potassium cyanide and heating the mixture as uniformly as possible, the temperature being raised gradually (5 minutes) until the thermometer registered  $240^{\circ}$  for the vapor distilling over, and then raising it to  $240-300^{\circ}$  for 10 minutes. Washed with sodium hydroxide solution, the crude liquid distillate amounted to 2.5 g.

20 g. of the crude nitrile so obtained were distilled with steam, the yellow, oily distillate collected with ether, dried with calcium chloride, and fractioned. The first fractions (below  $200^{\circ}$ ) were obviously cymene; from  $200$  to  $255^{\circ}$ , 5.5 g. of impure nitrile were collected as a pale yellow liquid. Kreyser<sup>5</sup> gives the b. p. of the nitrile as  $244-6^{\circ}$ . This impure

<sup>1</sup> *J. prakt. Chem.*, [2] **15**, 247 (1877).

<sup>2</sup> Compare *J. Chem. Soc.*, **79**, 397 (1901); *Ber.*, **31**, 3276 (1898).

<sup>3</sup> *Gazz. chim. ital.*, **5**, 30 (1875).

<sup>4</sup> *Ibid.*, **9**, 400 (1879).

<sup>5</sup> *Ber.*, **18**, 1714 (1885).

nitrile was saponified by boiling it with alcoholic potassium hydroxide solution under a reflux condenser. When the heating was continued for about 24 hours, the product was almost exclusively the amide; longer heating gave increasing amounts of the acid.

The amide so obtained crystallized from water in colorless, glassy needles, m.  $138-41^{\circ}$  (corr.), and this m. p. could not be altered either by further crystallization or by fractional crystallization. Paterno and Fileti give the m. p. of their amide as  $138-9^{\circ}$  (corr.). The above amide, m.  $138-41^{\circ}$ , mixed with some amide of the 2-acid prepared from the chloride of the 2-acid, showed a m. p. of  $139-44^{\circ}$  (uncorr.); but, when mixed with the amide of the 3-acid, melted at  $121-32^{\circ}$  (uncorr.).

A small amount of cymene 2-carboxylic acid recovered in the above saponification, when recrystallized from dilute alcohol, showed a m. p.  $69-71^{\circ}$ , and when mixed with some pure 2-acid, m.  $69-72^{\circ}$ . The acid obtained by Paterno and Spica, therefore, by fusing the amide with potassium hydroxide, or by heating it with concentrated hydrochloric acid at  $180^{\circ}$ , was manifestly an impure cymene 2-monocarboxylic acid.

## II. *p*-Cymene 3-Carboxylic Acid.

**3-Bromocymene** has been prepared by Von Gerichten<sup>1</sup> and by Fileti and Crosa<sup>2</sup> by the action of  $\text{PBr}_5$  upon thymol. The latter give the b. p. as  $232-3^{\circ}$  (in the vapor) at 740.9 mm. (reduced to  $0^{\circ}$ ). Kelbe and Koschnitzky<sup>3</sup> claimed to have obtained this bromocymene from what they believed to be the 3-bromocymene-6-sulfo acid; but Claus and Christ<sup>4</sup> were of opinion that the product obtained by these investigators was in reality the 2-bromocymene.

The 3-bromocymene used in the following experiments was made by the method of Fileti and Crosa from thymol and  $\text{PBr}_5$ , and our yields checked those of these investigators (60%). The purified material showed a b. p.  $231.2-233.2^{\circ}$  (corr.). It was found, further, that any increase in the amount of  $\text{PBr}_5$  above that given by Fileti and Crosa resulted in a decreased yield.

An effort was made to help the yield by the addition of fused zinc bromide to the reaction mixture, since Dehn and Davis<sup>5</sup> have shown that the presence of zinc chloride materially increases the amount of alkyl halide obtainable from the alcohol and phosphorus halide, but the results were unsatisfactory. The effect of fused zinc bromide upon tri-thymyl phosphate was also studied, in the hope that thereby the bromocymene might be secured directly from the phosphate which is a by-product in

<sup>1</sup> *Ber.*, 11, 1719 (1878).

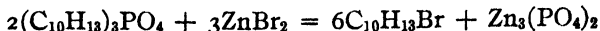
<sup>2</sup> *Gazz. chim. ital.*, 16, 292 (1886).

<sup>3</sup> *Ber.*, 19, 1731 (1886).

<sup>4</sup> *Ibid.*, 19, 2165 (1886).

<sup>5</sup> *THIS JOURNAL*, 29, 1328 (1907).

the preparation of the bromocymene from thymol and  $\text{PBr}_5$ . It was expected that reaction might occur in the following sense:



The results were disappointing, for on distilling 60 g. of the tri-thymyl phosphate and 40 g. anhydrous zinc bromide (in intimate mixture) from a retort, but small amounts of the bromocymene were formed.

As has been pointed out already, in the foregoing, 3-bromocymene is also produced in the direct bromination of cymene.

**p-Cymene 3-Carboxylic Acid**,  $\text{C}_{10}\text{H}_{18}\text{COOH}$ , was prepared from 3-bromocymene, magnesium and  $\text{CO}_2$ , practically as described already for the isomeric 2-acid. In a typical experiment, 119 g. 3-bromocymene, 13.6 g. magnesium, and 300 cc. absolute ether, were treated for 16 hours with excess of  $\text{CO}_2$  under pressure, at a temperature below  $-5^\circ$ . The yield of crude acid was 55 g., or approximately 55% of the theoretical.

Purified by crystallization from dilute alcohol, this acid forms colorless, glassy needles, m.  $84^\circ$  (corr.); practically insoluble in cold water; difficultly soluble in hot water; more or less soluble in ligroin, benzene, xylene, methyl or ethyl alcohols, chloroform, carbon tetrachloride, acetone, carbon disulfide, dilute acetic acid or in ethyl acetate. It does not sublime, but distils at ordinary pressure with but little decomposition, b.  $285^\circ$  (corr.), and the distillate immediately solidifies. It volatilizes quite easily with steam, and when distilled with excess of soda lime gives cymene again. The unsatisfactory m. p. often found for this acid is due in most cases to moisture, rather than to the presence of other contaminants. For a sharp m. p., the acid must be dried for several days in a vacuum desiccator over calcium chloride, or heated for a short time at  $65\text{--}70^\circ$ .

Subs. 0.1800, 0.2034:  $\text{CO}_2$ , 0.4891, 0.5531;  $\text{H}_2\text{O}$ , 0.1264, 0.1455. Calc. for  $\text{C}_{10}\text{H}_{18}\text{O}_2$ : C, 74.16; H, 7.87. Found: C, 74.11, 74.16; H, 7.80, 7.95.

A cryoscopic molecular-weight determination in acetic acid gave the figures 172 and 175, the calculated figure being 178.

**Sodium Salt**,  $\text{NaA}$ .—The barium salt was dissolved in hot water, and a dilute solution of sodium carbonate added carefully as long as it caused a precipitate. The precipitated barium carbonate was then filtered out and the filtrate concentrated. As the salt is very soluble in water, this concentration must be carried practically to dryness. The salt is thus obtained as a white, pulverulent solid, which appears to deliquesce at  $10^\circ$ , but loses this water again at room temperature. It crystallizes without water of crystallization.

Anhydrous salt, 0.3100:  $\text{Na}_2\text{SO}_4$ , 0.1147. Calc. for  $\text{C}_{10}\text{H}_{18}\text{O}_2\text{Na}$ : Na, 11.50. Found: Na, 11.99.

**Potassium Salt**,  $\text{KA}$ .—A dilute solution of potassium hydroxide was treated with excess of the pure 3-acid, the excess of acid filtered out of the



cold solution, and the filtrate evaporated. The salt is very easily soluble in water, but carries no water of crystallization. It is a white powder.

Anhydrous salt, 0.3226:  $K_2SO_4$ , 0.1280. Calc. for  $C_{11}H_{13}O_2K$ : K, 18.09. Found: K, 17.82.

**Barium Salt**,  $BaA_2 \cdot 2H_2O$ .—Some of the free acid was suspended in hot water and digested for four or five hours with excess of barium carbonate at  $100^\circ$ . The acid dissolved gradually. The excess of barium carbonate was removed, and the filtrate concentrated to small volume, the salt then separating as a colorless solid, quite easily soluble in hot water.

Subs. 0.3412, heated to constant weight at  $110^\circ$ :  $H_2O$ , 0.0237. Calc. for  $(C_{11}H_{13}O_2)_2Ba \cdot 2H_2O$ :  $H_2O$ , 6.83. Found:  $H_2O$ , 6.94.

Anhydrous salt, 0.3146:  $BaSO_4$ , 0.1476. Calc. for  $(C_{11}H_{13}O_2)_2Ba$ : Ba, 27.9. Found: Ba, 27.6.

**Calcium Salt**,  $CaA_2 \cdot 2H_2O$ .—This salt was prepared in the same manner as the above Ba salt. It is much less soluble in water than the latter, and only slightly more soluble in hot than in cold water, separating in imperfect crystals.

Subs. 0.2882, dried to constant weight at  $110^\circ$ :  $H_2O$ , 0.0238. Calc. for  $(C_{11}H_{13}O_2)_2Ca \cdot 2H_2O$ :  $H_2O$ , 8.37. Found:  $H_2O$ , 8.26.

Anhydrous salt, 0.2644:  $CaSO_4$ , 0.0892. Calc. for  $(C_{11}H_{13}O_2)_2Ca$ : Ca, 10.15. Found: Ca, 9.96.

**Copper Salt**,  $CuA_2$ .—A copper acetate solution was added carefully to a hot aqueous solution of the calcium salt of the acid. The copper salt separated as an amorphous, light blue precipitate, which was filtered out, washed and dried. It is practically insoluble in water, but quite soluble in hot alcohol or in hot benzene, and crystallizes from alcohol in greenish blue microscopic needles, without water of crystallization.

**Silver Salt**,  $AgA$ .—This was prepared in the same manner as the silver salt of the 2-acid. It is colorless, apparently fairly stable in the light, and is somewhat soluble in water.

Subs. 0.2595, 0.2033: Ag, 0.0982;  $CO_2$ , 0.3487;  $H_2O$ , 0.0851. Calc. for  $C_{11}H_{13}O_2Ag$ : Ag, 37.87; C, 46.33; H, 4.56. Found: Ag, 37.84; C, 46.77; H, 4.65.

**Methyl Ester**,  $C_{10}H_{13} \cdot COOCH_3$ .—17 g. of the 3-acid were dissolved in a small excess of 10% potassium hydroxide solution, 23 g. of dimethyl sulfate added, and the mixture shaken vigorously for three hours. It was then heated for an hour on the water bath, to decompose any unchanged dimethyl sulfate, cooled, made slightly alkaline with potassium hydroxide and distilled with steam. The ester came over slowly as a colorless, heavy oil. It was collected with ether, the ethereal solution dried with calcium chloride, the ether distilled off and the residue fractionated at 13.5 mm. (reduced to  $0^\circ$ ), most of the ester (6.3 g.) then coming over at  $128-9^\circ$ , as a colorless liquid, with a characteristic pleasant odor.

Upon acidifying the residue from the steam distillation, 3.2 g. of the acid were recovered, its formation being probably referable to hydrolysis during the distillation with steam.

Subs. 0.1938:  $\text{CO}_2$ , 0.5324;  $\text{H}_2\text{O}$ , 0.1436. Calc. for  $\text{C}_{12}\text{H}_{16}\text{O}_2$ : C, 75.00; H, 8.33. Found: C, 74.92; H, 8.23.

**Ethyl Ester.**—15 g. of the acid were dissolved in a slight excess of potassium hydroxide solution, 25 g. (two mols) of diethyl sulfate added, the mixture shaken mechanically for three hours, and finally heated for an hour at  $100^\circ$ , to decompose the excess of diethyl sulfate. The ester separated as a pale yellowish oil. The mixture was made alkaline with KOH, the ester extracted with ether, the ether dried with calcium chloride, the solvent distilled off, and the residue fractioned under reduced pressure, collecting the fraction b.  $141-2^\circ$  at 13.5 mm. (corr.).

The product was a colorless oil, of pleasant odor, similar to that of the methyl ester but rather stronger. By acidifying the aqueous solution, after the ether extraction, some of the original acid was recovered.

Subs. 0.2059, 0.1413:  $\text{CO}_2$ , 0.5547, 0.3807;  $\text{H}_2\text{O}$ , 0.1596, 0.1100. Calc. for  $\text{C}_{12}\text{H}_{16}\text{O}_2$ : C, 75.72; H, 8.74. Found: C, 73.47, 73.48; H, 8.61, 8.65.

The product was, therefore, somewhat impure, the source of this contamination being possibly the commercial diethyl sulfate employed.

**Phenyl Ester.**—2.3 g. phenol (theory 2.1) were dissolved in 15 cc. pyridine, and 4.2 g. acid chloride added gradually with shaking and cooling. The solution soon turned red, and a white precipitate separated of pyridine hydrochloride. After standing overnight in the ice box, the mixture was poured into cold dilute sulfuric acid. An oil collected, which was washed thoroughly with water, to remove all pyridine, then with dilute caustic alkali, to remove any 3-acid, after which it was taken up in ether, the solution dried with calcium chloride, the ether evaporated and the residue fractioned at 22.5–24.5 mm. when it distilled at  $199-208^\circ$ . It remained a liquid, and all attempts to congeal it by freezing, or by leaving it in a desiccator over concentrated  $\text{H}_2\text{SO}_4$ , failed. The inference, therefore, is that this ester is either a liquid at ordinary temperatures or a low-melting solid.

The Acid Chloride was prepared in much the same way as the chloride of the 2-acid. The yield was 93% or better.

In the pure state, it is a colorless mobile liquid of penetrating odor, b.  $115-6^\circ$  at 9.2 mm., or  $128-9^\circ$  at 20.1 mm., and is slowly hydrolyzed by cold water.

**Acid Amide.**—3 g. of the acid chloride were dissolved in a small amount of anhydrous ether and a rapid current of dry ammonia past into the solution, cooling the vessel with a freezing mixture. An abundant white precipitate rapidly separated. The solution, saturated with ammonia, was allowed to stand for a short time and then filtered. Very little

amide remained in the ethereal filtrate. The original precipitate was washed thoroughly with water, to eliminate ammonium chloride, dried and crystallized from benzene. Yield before crystallization, 93%.

The pure amide crystallizes from benzene in radiating clusters of minute colorless, silky needles which mat together, and *m.* 137.5° (corr.). It is but slightly soluble in cold ligroin, benzene, ether or carbon tetrachloride; somewhat soluble in hot water; quite soluble in methyl or ethyl alcohol or in chloroform; and crystallizes well from either ligroin, benzene or carbon tetrachloride.

Subs. 0.2419: N, 16.82 cc. at 21° and 753 mm. Calc. for  $C_{11}H_{18}ON$ : N, 7.91. Found: N, 7.81.

**Acid Anilide.**—A dry ether solution of 3 g. of the acid chloride was added gradually, with shaking and cooling, to a dry ether solution of 6 g. aniline (4 mols.). A colorless precipitate appeared, and heat was liberated in the reaction. After standing overnight, the mixture was filtered and anilide was found both in the original precipitate and in the ethereal filtrate. From the latter, it was recovered by simple evaporation of the solvent; from the former, by washing with water, to remove aniline salt. The two lots thus secured were united, washed with a little dilute hydrochloric acid, to eliminate final traces of aniline, then with water, and dried. Yield, 74%.

The anilide is quite soluble in methyl alcohol, ethyl alcohol, ether, benzene, or chloroform, and but slightly soluble in water. It can be crystallized from ligroin, carbon tetrachloride or dilute alcohol. From the latter, it separates in beautiful colorless, silky needles, *m.* 151° (corr.).

Subs. 0.3350, 0.2722: N, 17.1 cc. at 19° and 751 mm.; 13.1 cc. at 18.5° and 762 mm. Calc. for  $C_{17}H_{19}ON$ : N, 5.53. Found: N, 5.78, 5.53.

**Sym.-3,3'-Dimethyl-6,6'-diisopropyl Dibenzoylhydrazine**,  $C_{10}H_{13}.CO.NH.NH.CO.C_{10}H_{13}$ .—The procedure for the synthesis of this hydrazine was the same as in the case of the analogous derivative of the 2-acid, using 10 g. of the acid chloride and 11 g. of 50% aqueous hydrazine hydrate solution. The crude product was washed with water, to remove hydrazine salt, and then with dilute sodium hydroxide solution, to eliminate any 3-acid. Acidification of the alkaline washings showed that practically none of the acid chloride had been hydrolyzed. Yield of crude diacyl hydrazine, 93%.

The pure compound crystallized in fine, colorless, silky needles, from alcohol, and *m.* 213.5° (corr.). It is very slightly soluble in ether, slightly soluble in chloroform or acetic acid, and moderately soluble in methyl alcohol, ethyl alcohol, benzene or acetone.

Subs. 0.1645: N, 11.90 cc. at 21° and 753 mm. Calc. for  $C_{22}H_{28}O_2N_2$ : N, 7.95. Found: N, 8.12.

$\alpha,\alpha'$ -3,3'-Di-*p*-cymyl-[*bb*<sub>1</sub>]-furodiazole was obtained by heating 2.5

g. of the above diacyl hydrazine at  $200^{\circ}$  or higher for about two hours, cooling, and extracting with benzene. The insoluble residue, 0.5 g. in amount, proved to be unchanged diacyl hydrazine. The benzene solution was boiled with boneblack, filtered, and the benzene evaporated, leaving behind 1.3 g. of the furodiazole sought.

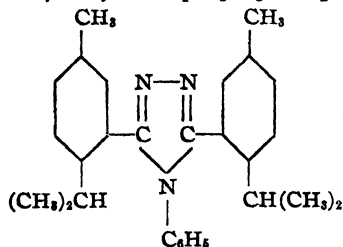
Crystallized from methyl alcohol, this diazole forms long, colorless, silky needles, much like the corresponding derivative of the 2-acid, and m.  $132.5^{\circ}$  (corr.). It is insoluble in water, slightly soluble in methyl alcohol or ethyl alcohol; quite soluble in benzene, benzine, chloroform, ether or acetone.

Subs. 0.1739: N, 12.9 cc. at  $20.5^{\circ}$  and 750.7 mm: Calc. for  $C_{22}H_{20}ON_2$ : N, 8.38. Found: N, 8.32.

An attempt to obtain the hydrazide chloride by the action of  $PCl_5$  upon the diacyl hydrazine, as described by Stollé<sup>1</sup> gave a final product composed of the furodiazole mixed with the hydrazide chloride sought, but the latter is apparently so unstable and reactive that our efforts to separate it in the pure state were fruitless. That it was present in the mixture was demonstrated by the amount of halogen found, the liberation of HCl during the attempted purification, and the production therefrom of the pyrrodiazole noted beyond.

The action of  $P_2S_5$  upon the diacyl hydrazine likewise yielded a mixture composed largely of the furodiazole, and from which no pure thiodiazole could be isolated. The difficulty in all these reactions is the ease with which the diacyl hydrazine loses water and goes over to the furodiazole condition.

**$\alpha, \alpha'-3,3'$ -Di-*p*-cymyl-N-phenyl-[*bb*<sub>1</sub>]-pyrrodiazole,**



—6 g. of the mixture of hydrazide chloride

and furodiazole obtained from the diacyl hydrazine and  $PCl_5$  by the method noted above, were warmed gradually to  $170^{\circ}$  and kept at that temperature (thermometer in melt) for half an hour. The mass fused slowly and quietly and on cooling formed a bluish green semisolid melt. It was washed thoroughly with dilute hydrochloric acid, to remove aniline, and then with ether, to remove the furodiazole. The residue was crystallized repeatedly from dilute alcohol, and the pyrrodiazole thus obtained in small compact, colorless, glassy crystals, m.  $182.5^{\circ}$  (corr.).

<sup>1</sup> *J. prakt. Chem.*, [2] 73, 288 (1906); 74, 1, 13 (1906); see also Thoma, *Inaug. Diss.*, Heidelberg, 1904.

It is practically insoluble in water or benzene, moderately soluble in ether, and quite soluble in benzene, methyl alcohol, ethyl alcohol, chloroform, carbon tetrachloride or acetone.

Subs. 0.1360: N, 12.7 cc. at 22° and 751 mm. Calc. for  $C_{22}H_{21}N_3$ : N, 10.27. Found: N, 10.45.

From the ether washings of the crude product, there were isolated both the furodiazole (m. 132.5°, corr.) and the above pyrrodiazole (m. 182.5°, corr.).

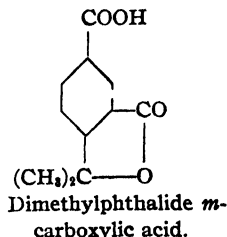
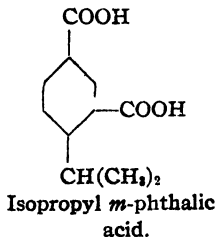
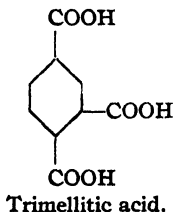
**3-Methyl-6-isopropyl Hippuric Acid**,  $CH_3(C_2H_7)C_6H_3.CO.NH.CH_2-COOH$ .—2 g. of the acid chloride were added to a concentrated aqueous solution of 2 g. glycine, then a little dilute sodium hydroxide solution, and the mixture shaken mechanically, testing from time to time and adding more alkali as needed to maintain a feebly alkaline reaction. In two hours the acid chloride had essentially all dissolved and the mixture was acidified cold with dilute hydrochloric acid. The white precipitate which separated was removed, washed with ligroin, to rid it of any 3-acid, and crystallized by dissolving it in a small quantity of alcohol, then pouring in several volumes of boiling water and allowing to stand. The colorless pearly scales resulting were thoroughly washed with cold ligroin, and then m. 205.5° (corr.).

As thus purified, this hippuric acid derivative is soluble in methyl alcohol, ethyl alcohol or acetone; much less soluble in chloroform or ether; still less in benzene or carbon tetrachloride, and practically insoluble in water or ligroin.

Subs. 0.1743: N, 9.45 cc. at 22° and 746.5 mm. Calc. for  $C_{18}H_{17}O_2N$ : N, 5.96. Found: N, 6.00.

The use of heat to hasten this reaction is objectionable, as it causes too much hydrolysis of the acid chloride with consequent falling off in the yield of hippuric derivative.

**Oxidation of Cymene 3-Carboxylic Acid**.—Preliminary experiments indicated the formation of the following acids on oxidation of cymene 3-carboxylic acid:



By oxidation with dilute (1 : 1) nitric acid, an acid was obtained, m. 218–24°, believed to be trimellitic acid, the m. p. of which is variously, stated in the literature from 217 to 225°.

With alkaline potassium permanganate, an acid resulted, m.  $233-5^{\circ}$  (uncorr.), apparently isopropyl *m*-phthalic acid (m.  $236^{\circ}$ ) and, by further oxidation, an acid, m.  $195-8^{\circ}$ , which gave an impure ethyl ester, m.  $102-5^{\circ}$ . The latter is, therefore, probably the dimethylphthalide *m*-carboxylic acid, which m.  $205-6^{\circ}$ , and its ethyl ester at  $105-6^{\circ}$ .

Unfortunately, the reactions were not carried out with enough material to adequately purify these oxidation products and more definitely establish their identity, but it is hoped to complete this part of the work at a later date.

**Reduction of Cymene 3-Carboxylic Acid.**—A solution of the acid in glacial acetic acid was mixed with a solution of colloidal platinum, and the resulting homogeneous solution shaken mechanically for 20 hours while it was subjected to treatment with hydrogen at 13 lbs. pressure. No reduction occurred, the original acid being recovered unchanged. Experiments on the reduction of an amyl alcohol solution of the acid by metallic sodium are under way and will be reported later.

#### Summary of Results.

1. The syntheses of *p*-cymene 2-carboxylic acid and of *p*-cymene 3-carboxylic acid, have been accomplished from the corresponding bromo cymenes, and numerous derivatives of these acids prepared and studied.

2. The statements in the literature concerning cymene 2-carboxylic acid and its salts have been tested and corrected. The following hitherto unknown derivatives have been prepared: methyl ester, ethyl ester, acid chloride, acid anilide, diacyl hydrazine, the furodiazole condensation product from the latter, the cymyl hippuric acid and its ethyl ester.

3. Cymene 3-carboxylic acid is entirely new. In addition to the free acid, the following derivatives have been synthesized and examined: Na, K, Ca, Ba, Cu and Ag salts, methyl ester, ethyl ester, phenyl ester, acid chloride, acid amide, acid anilide, diacyl hydrazine, the furo- and *N*-phenyl pyrrodiazole condensation products from the latter, and the cymyl hippuric acid.

4. The bromination product of cymene has been shown to be a mixture of 2- and 3-bromo derivatives, and not a pure 2-bromo derivative as hitherto assumed.

NEW YORK, N. Y.

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[CONTRIBUTION FROM THE MELLON INSTITUTE OF THE UNIVERSITY OF PITTSBURGH.]

### THE HYDROLYSIS OF CHLOROPENTANES AS AFFECTED BY HIGH PRESSURE: SYNTHETIC FUSEL OIL.

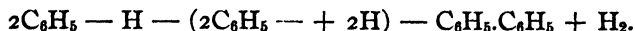
By HARRY ESSEX, HAROLD HIBBERT AND BENJAMIN T. BROOKS.

Received May 6, 1916.

The recent work of Meyer and Bergius<sup>1</sup> on the conversion of chlorobenzene and chloronaphthalene into phenol and  $\alpha$ -naphthol, respectively,

<sup>1</sup> *Ber.*, 47, 3155 (1914).

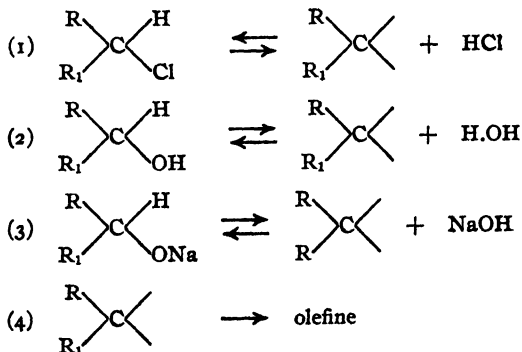
by heating the chlorides with aqueous alkalis at about  $300^{\circ}$  and 1500 pounds<sup>1</sup> pressure, showed that the yields were increased by pressure and to a very striking degree. We have employed similar conditions and also much higher pressures with chloropentanes with the object of studying their conversion into the amyl alcohols. Obviously the two cases show several marked points of difference. Benzene dissociates on heating to about  $550^{\circ}$ , giving hydrogen and diphenyl,<sup>1</sup>



The temperature at which the dissociation of chlorobenzene first becomes appreciable must be somewhat lower than this, although Meyer and Bergius heated chlorobenzene with water vapor at atmospheric pressure at  $500^{\circ}$  without any noticeable reaction.

In the presence of considerable excess of 15% NaOH solution at  $300^{\circ}$ , Meyer and Bergius obtained first diphenyl ether and finally, after longer heating, nearly theoretical yields of phenol. Dilute alkalis, lime, sodium carbonate and borax solutions had very little effect on chlorobenzene under the same conditions of pressure and temperature. Our findings on the behavior of chloropentane differ very markedly from their results. With the alkyl chloride, we obtained practically the same yields of alcohol with sodium carbonate as with caustic soda and even larger yields with sodium acetate than with sodium carbonate under conditions otherwise substantially the same. The amount of diamyl ether formed was usually very small, never exceeding 8%. When glacial acetic acid is employed as a solvent, the relatively more stable amylacetate is obtained in much larger yields and at much lower pressures.




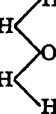


These results appear to be explained in a very satisfactory manner by Nef's<sup>2</sup> theory of the manner in which the alkyl halides dissociate and then react with other substances by addition.



<sup>1</sup> Cf. Engler, *Das Erdöl*, Vol. I, 576.

<sup>2</sup> THIS JOURNAL, 26, 1570 (1904); *Ann.*, 309, 126; 318, 1.

The relative ease with which some of the compounds of the ethane series, the hydrocarbon, alkyl chloride, alcohol, ether and sodium alcoholate appreciably decompose is shown in the following:<sup>1</sup>

Substance.	Temperature.
Ethane $\text{CH}_3\text{CH}$ 	800°
Ethyl alcohol $\text{CH}_3\text{CH}$ 	650°
Ethyl chloride $\text{CH}_3\text{CH}$ 	510-530°
Ethyl ether $\text{CH}_3\text{CH}$ 	550°
Sodium ethylate $\text{CH}_3\text{CH}$ 	250°
Ethyl acetate $\text{CH}_3\text{CH}$ 	"low red heat" <sup>2</sup>

Comparative data for the corresponding compounds of the *n*-pentane series are lacking. The relative stability of the primary derivatives of *n*-pentane is undoubtedly of the same order, with respect to one another, as in the ethane series. The same probably holds in the series of secondary derivatives. The chloropentanes employed in this work were prepared from petroleum pentane, as herein described, and consisted of the 1, 2 and 3 monochloro derivatives.

The effect of caustic alkali in producing increased yields of amylene, as compared with sodium carbonate, borax and sodium acetate, finds a ready explanation in the low dissociation temperature of the sodium alcoholate. This would have the effect of increasing the concentration of the dissociated methene, which has the result of increasing the amount of olefine formed,<sup>3</sup> as is expressed by Equations 3 and 4. To produce

<sup>1</sup> Nef, *Loc. cit.*

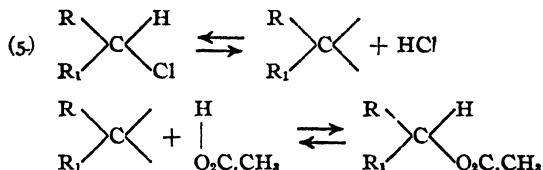
<sup>2</sup> Oppenheim and Precht, *Ber.*, 9, 325 (1876).

<sup>3</sup> Nef, *Ann.*, 318, 1 (1901) has shown that when isoamyl chloride, bromide and iodide are heated with alcoholic sodium ethylate, the chloride gives the greatest yield of isoamyl ethyl ether and the iodide the largest yield of amylene, which he explains by assuming that the rate of the addition of alcohol to the dissociated methene is not sufficient to combine with the latter as fast as formed, resulting in its partial rearrangement to amylene.



large yields of amyl alcohol in the presence of caustic alkali, the temperature should not exceed that at which the dissociation of sodium amylate takes place to a sensible degree. But this temperature is so much lower than the temperature at which the dissociation of the chloride becomes appreciable that the formation of alcohol or alcoholate is extremely slow. Higher yields of alcohol are therefore obtained when employing temperatures sufficient to dissociate the chloride at a fairly rapid rate,  $215^{\circ}$ , and solutions of a weak base or the alkali salt of a very weak acid, so that the HCl split off is taken up. It should be pointed out that, excepting the olefine, the alcohol is the most stable substance in the system.

In the presence of glacial acetic acid much higher yields of alkyl acetate than of alcohol are obtained when water is employed as the solvent, the conditions of temperature and pressure being the same in the two cases.<sup>1</sup>



This may be due to the fact that glacial acetic acid is more highly dissociated than water. It would then be expected that dissociated methene of a given concentration would react more rapidly with acetic acid than with water, or, in other words, a lower temperature (lower concentration)

of  $\begin{array}{c} \text{R} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{R}_1 \end{array}$  should suffice to produce a given yield of product, *i. e.*, acetate. Higher yields are obtained when anhydrous sodium acetate is added to the mixture than when glacial acetic acid alone is employed, the function of the sodium acetate apparently being to take up the hydrogen chloride with the formation of sodium chloride and the liberation of acetic acid.

It now remains to consider the effect of pressure on the two systems chloropentane and water; and chloropentane, water and alkali. It is obvious that in the case of chloropentane alone the effect of increased pressure will be to prevent the dissociation as indicated in Equation 1. Increased pressure should effect the dissociation of the alcohol, Equation 2, in the same direction. As has been noted above, the addition of caustic alkali causes increased formation of olefine at the expense of alcohol, which we interpret as being brought about by the effect of caustic alkali in increasing the concentration of  $\begin{array}{c} \text{R} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{R}_1 \end{array}$ . Increase of pressure

should, therefore, tend to confine the reactions which take place to

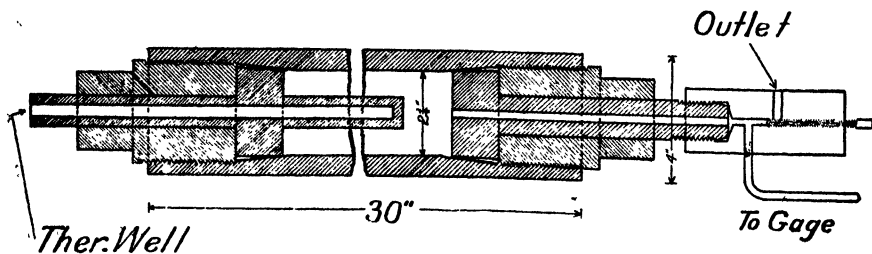
<sup>1</sup> The data on these experiments are reserved for later publication.

those expressed by (1) and (2). If the volume change of Equation 2 is greater than that of Equation 1, then increase in pressure should cause the alcohol to become relatively more stable with respect to the chloride; in other words, the difference of temperature between the "decomposition temperature" of amyl alcohol and amyl chloride becomes greater at high pressures. Probably a similar difference in stability would be found in the case of ethyl chloride and ethyl alcohol at high pressure.

We have found that heating monochloropentane with water vapor at atmospheric pressure until decomposition becomes appreciable leads to the formation of amylene almost exclusively. In the same way, Meyer and Bergius<sup>1</sup> found that by heating chlorobenzene and water vapor at atmospheric pressure to temperatures at which decomposition could be noted, namely, nearly 600°, only 10% of phenol was formed after "several hours" heating in an apparatus arranged for circulating and repeatedly heating the vapors.

### Experimental.

The pressure bomb employed was very simple in construction, a piece of seamless steel tubing 30 inches long, internal diameter 2.5 inches and 0.75 inch thickness of wall. The open ends were carefully machined and threaded so as to be closed by conical plugs forced in to place by heavy forged steel screw plugs. The conical plugs, sealing the interior chamber, were kept centered during the closing operation by the centering pins passing through the screw plugs, and were tapered a few degrees less than the seat machined in the tube, as shown in the sketch. A valve was provided for escape of gas, such as CO<sub>2</sub>, produced in some of the reactions. The temperature in the bomb was read by a thermocouple placed in the thermometer-well shown and the pressure indicated on an hydraulic gage, reading to ten thousand pounds per square inch. The heating was accomplished electrically by means of a simply constructed nichrome wire resistance furnace and it was found possible to control the temperature in the bomb to about  $\pm 2^\circ$  of the desired point. In order to attain pressures higher than were given by water and the reaction products, ether was added in some cases, and in many cases the bomb was filled completely with the liquid mixture.



<sup>1</sup> Loc. cit.

Meyer and Bergius mention the use of cuprous chloride as a catalyst accelerating the reaction in the case of chlorobenzene. In our work with amyl chlorides, we were unable to detect any effect in the rate or character of the reaction which could be attributed to this substance. Basic lead carbonate was also tried, but without result.

In working up the resulting reaction mixtures, the liquid layer was separated, washed with water, dried with anhydrous sodium sulfate and fractionated. The fusel oil distils over in the fraction boiling above  $115^{\circ}$ , but, since appreciable quantities distil with the fraction-boiling point  $100-115^{\circ}$ , this fraction was acetylated and refractionated. The acetylated product obtained, boiling above  $115^{\circ}$ , was then calculated back to amyl alcohol. The unchanged chlorides, contained in the fusel oil fraction, were found by analyzing for chlorine by the method of Drogin and Rosanoff<sup>1</sup> and making the necessary correction. That the polymerization of the amylene, formed as a by-product, to diamylene occurs to slight extent under the conditions prevailing in these experiments is indicated by the following distillation results:

#### FRACTIONAL DISTILLATION OF ALCOHOL PORTION.

Distillation temperatures.	Quantity per cent.
$115-125^{\circ}$ .....	22.8
$125-140^{\circ}$ .....	53.1
$140-150^{\circ}$ .....	2.7
$150-170^{\circ}$ .....	11.7 <sup>2</sup>
$170-190^{\circ}$ .....	5.5
Residue and loss .....	4.2

That the large yields, generally obtained in the experiments in which ether was added to the reaction mixture, are due primarily to the resulting higher pressure and not to any catalytic or solvent action is indicated by the equally large yields in those experiments in which the conditions were substantially the same, but containing no ether in the reaction mixture, and also by the fact that, comparing a series in which ether was introduced, those carried out at the higher pressures gave much higher yields of alcohol, other factors remaining the same.

#### WITH SODIUM HYDROXIDE OR POTASSIUM HYDROXIDE.

Mixture in bomb.	Time of heating.	Temperature.	Maximum pressure.	Yield of fused oil.
100 g. chloride; 5 g. $\text{Cu}_2\text{Cl}_2$	8 hrs.	$190^{\circ}$	240 lbs.	0.0%
212 cc. 25% sol. KOH				
213 g. chloride; 20 g. $\text{Cu}_2\text{Cl}_2$	$8\frac{1}{2}$ hrs.	$250^{\circ}$	1200 lbs.	20.5%
740 cc. 25% sol. NaOH				

<sup>1</sup> THIS JOURNAL, 38, 711 (1916).

<sup>2</sup> This fraction also contained diamyl ether.

## WITH SODIUM HYDROXIDE OR POTASSIUM HYDROXIDE.

Mixture in bomb.	Time of heating.	Temperature.	Maximum pressure.	Yield of fused oil.	Unchanged chlorides
213 g. chloride; 20 g. $\text{Cu}_2\text{Cl}_2$	9 hrs.	300°	3200 lbs.	20.0%	
480 cc. 16.5% sol. NaOH					
300 cc. ether					
213 g. chloride; 20 g. $\text{Cu}_2\text{Cl}_2$	9 hrs.	250°	4200 lbs.	33.0%	
480 cc. 16.5% sol. NaOH					
500 cc. ether					
213 g. chloride; 20 g. $\text{Cu}_2\text{Cl}_2$	8 hrs.	210°	3300 lbs.	38.0%	
80 g. NaOH (580 cc. sol.)					
500 cc. ether					

## WITH SODIUM CARBONATE.

213 g. chloride	30 hrs.	150°	Below 200 lbs.	0.0%	
424 cc. 25% $\text{Na}_2\text{CO}_3$					
25 g. basic Pb carbonate					
213 g. chloride; 8 g. $\text{Cu}_2\text{Cl}_2$	8 hrs.	250°	1100 lbs.	13.6%	
424 cc. 25% sol. $\text{Na}_2\text{CO}_3$					
213 g. chloride	4 hrs. at 250° and	250-300°	1100-2100 lbs.	15.0%	
424 cc. 25% sol. $\text{Na}_2\text{CO}_3$	4 hrs. at 300°				
25 g. freshly pptd. basic Pb carbonate					
213 g. chloride, 200 cc. ether	8 hrs.	250°	1050 lbs.	9.0%	
424 cc. 25% sol. $\text{Na}_2\text{CO}_3$					
25 g. basic Pb carbonate					
213 g. chloride; 300 cc. ether	10 hrs.	250°	1400 lbs.	25%	
425 cc. 25% $\text{Na}_2\text{CO}_3$					
25 g. basic Pb carbonate					
300 g. chloride; 20 g. $\text{Cu}_2\text{Cl}_2$	11 hrs.	225°	4700 lbs.	36%	7%
149 g. $\text{Na}_2\text{CO}_3$ (596 cc. sol.)					
470 cc. ether					
260 g. chloride; 400 cc. ether	8 hrs.	250°	4700 lbs.	35%	
193 g. $\text{Na}_2\text{CO}_3$ (517 cc. sol.)					
34 g. $\text{Pb}(\text{OH})_2$					
290 g. chloride	17 hrs.	210°	3300 lbs.	37.5%	
215 g. $\text{Na}_2\text{CO}_3$ (577 cc. sol.)					
300 g. chloride; 460 cc. ether	8 hrs.	235°	6000 lbs.	51.2%	
223 g. $\text{Na}_2\text{CO}_3$ (596 cc. sol.)					
20 g. $\text{Cu}_2\text{Cl}_2$					

## WITH SODIUM ACETATE.

236 g. chloride; 20 g. $\text{Cu}_2\text{Cl}_2$	9 hrs.	250°	1400 lbs.	31%	
300 g. $\text{NaCH}_3\text{CO}_2$ (700 cc. sol.)					

## WITH WATER ALONE.

300 g. chloride; 20 g. $\text{Cu}_2\text{Cl}_2$	6 hrs.	250°	1700 lbs.	23%	
600 cc. $\text{H}_2\text{O}$					

[CONTRIBUTION FROM THE BIOCHEMISTRY LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

## BRAIN CEPHALIN. II. FATTY ACIDS.

By C. G. MACARTHUR AND L. V. BURTON.

Received April 1, 1916.

As has been stated in the previous article of this series,<sup>1</sup> there is some uncertainty as to what fatty acids are present in the cephalin molecule and considerable uncertainty as to the amounts of each.

**Preparation.**—In this work preparations have been made in several ways, some old, some new, to see whether there are consistent differences in the molecule depending on the method of preparation.

Cephalins (1), (2), (3) and (4) were prepared and purified as described in the previous paper. Another preparation, purified like cephalin (4), was further purified by dissolving in chloroform and precipitating with twice the solution's volume of absolute alcohol. The object of this treatment was to remove any trace of sphingomyelin that might still contaminate the product. The desiccated material was then emulsified in water and precipitated by an equal volume of acetone. The precipitate was further washed with acetone, placed in a vacuum desiccator and dried, then taken up in ether, centrifuged, and precipitated by acetone and dried. This will be referred to as cephalin (8). It is a light yellow powdery product, similar in appearance to cephalin (4).

**Percentage of Total Fatty Acids in Cephalin.**—To determine the percentage of total fatty acids in cephalin, one gram of the cephalin was hydrolyzed for 20 hours in a 1% hydrochloric acid solution. The fatty acid residue, after filtration, was dissolved in ether, filtered, and carefully evaporated to dryness in a weighed dish. It was dried over sulfuric acid till constant weight was obtained. By this method cephalin (1) (HCl purified) gave 0.670 g. of fatty acids. One gram of cephalin (4) gave 0.652 g. The fatty acids from another sample of cephalin (1) weighed 0.66 g. From this data it seems that 66% of cephalin is in the form of fatty acids. It is likely that these values are slightly high because there is a small amount of an unhydrolyzable substance that would be included in the total fatty acids.

### Quantitative Study.

Four grams (usually) of the cephalin were dissolved in 200 cc. of a 2% water potassium hydroxide solution. This was boiled for 20 hours under a reflux condenser, cooled and acidified with acetic acid. The fatty acids were filtered rapidly, washed three times with distilled water, then dissolved in dilute potassium hydroxide. The solution was now neutralized with acetic acid and an equal volume (about 150 cc.) of a 5% lead acetate solution added. The lead soaps were filtered through a

<sup>1</sup> MacArthur, *THIS JOURNAL*, 36, 2397 (1914).

hardened filter, washed three times, and dried with filter paper and then in a vacuum desiccator. The comparatively dry soaps were carefully placed in a flask and refluxed with about 150 cc. of freshly distilled ether for several hours until all the particles were finely divided. The contents of the flask were cooled and either filtered or centrifuged and washed with small amounts of ether. In some experiments better results were obtained by allowing this solution to stand a few hours in a tall cylinder and then siphoning off the clear solution. The residue was washed three times.

The saturated insoluble lead soaps were decomposed either by passing  $\text{H}_2\text{S}$  through the hot benzene solution, or by refluxing the lead soap with an ether and hydrochloric acid solution in the usual manner. Several repetitions of this procedure were necessary. The free acids were evaporated to dryness and weighed. This gave the total saturated acids. The product was then recrystallized several times from alcohol and acetone, and was ready for melting point and molecular-weight determinations and derivatives.

The unsaturated lead soaps were decomposed by shaking the ether solution with several portions of a dilute  $\text{HCl}$  solution. The ether solution was then washed with water, dried with anhydrous sodium sulfate, and filtered into a flask.

The solution of the unsaturated acids was cooled in ice water, and bromine added in small portions till an excess was present. They were allowed to stand overnight in ice bath in the ice box, then placed in a corked weighed centrifuge tube and the ether-insoluble bromine derivative centrifuged out. It was washed with ether several times, dried and weighed. From a bromine determination on this compound the amount of fatty acid in it could be calculated. The bromine determination also helped to identify the acid.

The ether solution of the ether-soluble bromine derivatives was placed in a separatory funnel and an excess of sodium thiosulfate added. The funnel was thoroughly shaken, allowed to stand, and then the water layer was drawn off. The ether was again treated with sodium thiosulfate. Finally it was washed with several portions of water, dehydrated with anhydrous sodium sulfate, filtered into a weighed beaker and carefully evaporated to dryness. The weight gave the amount of the ether-soluble bromine derivatives.

To separate these the mixture was extracted at room temperature several times with small portions of petroleum ether (b. p.  $30-50^\circ$ ). A white insoluble bromide remained. The petroleum ether solution was evaporated carefully to dryness and the residue again treated with small amounts of petroleum ether. A small portion remained undissolved. These two residues were united, dried and weighed. They represent the

petroleum-ether-insoluble bromine derivative. From the bromine determination the amount of free fatty acid was determined. This bromine value and the melting point were used to give an idea of the identity of the compound.

The petroleum ether solution was evaporated to dryness in a weighed beaker. This gave the petroleum-ether-soluble bromine derivative. As a rule this weighed residue was dissolved in acetone. There was a small amount of an acetone-insoluble saturated compound containing 1.3% nitrogen left, probably not fatty acid. The solution was evaporated and weighed. This gave the true weight of the liquid dibromide. From the amount of bromine in it the amount of the fatty acid could be calculated.

By the above procedure the following data were obtained:

TABLE I.

2 g. sheep cephalin (8). Calculated weight of acids = 1.32 g.

	Wt. of bromide.	Wt. of acid.	% of total acids.
Stearic acid.....	..	0.43	32.6
Oleic acid.....	1.14	0.73	55.4
Cephalinic acid.....	0.24	0.09	7.0
Clupanodonic acid.....	0.17	0.05	3.9
		<hr/>	<hr/>
		1.30	98.9

6 g. sheep cephalin (4). Calculated weight of acids = 3.96 g.

Stearic acid.....	..	1.21	30.6
Oleic acid.....	3.41	2.18	55.5
Cephalinic acid.....	0.64	0.26	6.5
Clupanodonic acid.....	0.49	0.16	4.0
		<hr/>	<hr/>
		3.73	96.6

3 g. beef cephalin (4). Calculated weight of acids = 1.98 g.

Stearic acid.....	..	0.58	29.3
Oleic acid.....	1.60	1.05	53.0
Cephalinic acid.....	0.36	0.15	7.5
Clupanodonic acid.....	0.21	0.07	3.5
		<hr/>	<hr/>
		1.85	93.3

In a few analyses the hydrolysis of the cephalin and the solution of the fatty acids in ether were carried out as above described. Instead of separating the saturated from the unsaturated acids, however, the ether solution was brominated and separated as before. The saturated acids will be in with the oleic bromide. The two were weighed together, then from a bromine determination on a fraction of this mixture the amount of oleic bromide and oleic acid could be calculated. The difference between the weight of oleic bromide and that of the mixture was assumed to be stearic acid. From the following data it will be noticed that the agreement is rather close with that of the lead method:

TABLE II.

3 g. sheep cephalin (4). Calculated weight of acids = 1.98 g.

	Wt. of bromide.	Wt. of acid.	% of total acids.
Stearic acid.....	..	0.55	27.8
Oleic acid.....	1.75	1.12	56.6
Cephalinic acid.....	0.45	0.18	9.0
Clupanodonic acid.....	0.23	0.07	3.5
		<hr/>	<hr/>
		1.92	96.9

**Discussion of Quantitative Experiments.**—A consideration of the data will show that there is no definite relationship between the amounts of the various acids in cephalin. Stearic acid comprises somewhat more than one-fourth of the total fatty acids. According to the generally accepted formula of cephalin, one-half of the cephalin would be present as stearic acid. Oleic acid constitutes about one-half of the total acids. Approximately one-tenth is cephalinic acid, and one-twentieth clupanodonic. It might be thought that one nitrogen constituent was present with each acid, thus giving a mixture of stearyl cephalin, oleyl cephalin, etc. There does not seem to be enough agreement, however, between the amounts of the nitrogenous compounds and the acids to warrant this assumption.

To explain the presence of these acids in such different amounts, it is best to assume that some of the cephalin molecules may have oleic and cephalinic acids, and still others stearic and cephalinic, etc. It is well known that ordinary fats are often thus mixed. It is reasonable, then, to suppose that a highly labile compound like cephalin may have varying fatty acids on any particular molecule. They may even be changing from molecule to molecule in the cephalin mixture.

It is exceedingly difficult to purify cephalin. It is next to impossible to separate the constituents of the mixture, even though some of the supposed cephalin molecules have such different acids as clupanodonic and stearic in them. Because of these facts one may think of cephalin as made up of several constituents more closely associated than a mixture but less so than a simple compound. It may be this power of forming comparatively firm association compounds that partially explains its peculiar importance in brain cell metabolism.

#### Identification of the Fatty Acids.

To obtain the individual fatty acids or their derivatives for identification, the same procedure was used in most cases as for the quantitative data. For a few experiments, in order to obtain larger amounts of the ether-insoluble and petroleum-ether-insoluble derivatives, 8 g. of the cephalin were hydrolyzed as described and all the free fatty acids dissolved in ether, then brominated and separated according to the above method. In this way the saturated acids went into the ether-soluble bromide fraction, and so did not interfere with the preparations sought.



**Stearic Acid.**—The somewhat impure saturated acid obtained from sheep cephalin (4) by the quantitative procedure described above gave a molecular weight of 289, a sample of sheep cephalin (1) gave 290.

(4) 0.1096 g. acid.....	3.7 cc. 0.1 <i>N</i> alk.	289 m. w.
(1) 0.2285 g. acid.....	7.8 cc. 0.1 <i>N</i> alk.	290 m. w.

These results were obtained by the usual procedure, dissolving the acid in a definite amount of alcohol and titrating with 0.1 *N* alkali. The number of cc. used in a control on an equal volume of alcohol was subtracted from the fatty acid value.

These impure samples were crystallized twice from alcohol and twice from acetone. The molecular weights then were 284.5 and 284.

(4) 0.2310 g. acid.....	7.95 cc. 0.1 <i>N</i> alk.	284.5 m. w.
(1) 0.2080 g. acid.....	7.15 cc. 0.1 <i>N</i> alk.	284.0 m. w.

This pure acid melted at 69°. Several other samples purified by crystallization from alcohol and acetone gave melting points varying from 68.8° to 69.2°.

The ethyl ester prepared in the usual way had a melting point of 33.4°.

Because the molecular weight of stearic acid is 284, its melting point is 69°, and ethyl stearate melts at 33.5° it may be concluded that stearic acid is the only saturated acid in cephalin in appreciable amounts. It was not determined what impurity present caused the high molecular weight of the impure stearic acid.

**Oleic Acid.**—The ether-soluble bromide fraction, after removal of the nitrogenous impurity by the latter's insolubility in acetone, was evaporated to dryness, dried over sulfuric acid and a bromine determination made on the heavy yellowish oil in the following way:

About 0.3 g. of the bromine derivative was carefully weighed into a nickel crucible. Ten grams of sodium hydroxide and 3 g. of potassium nitrate and a few drops of water were added. The crucible was covered and carefully heated to avoid spattering. Gradually the flame was raised till a melt was obtained. The heating was continued till the liquid was perfectly clear. It was allowed to cool partially, then was dissolved in water and made slightly acid with nitric acid. One cc. of 10% ferric ammonium sulfate was added and the solution titrated with 0.1 *N* silver nitrate and ammonium thiocyanide.

A few typical determinations out of many on the ether-soluble bromine fraction are given below:

	Bromine.
Sheep cephalin (8) 0.3000 g. bromine compound.....	36.5%
Sheep cephalin (4) 0.3891 g. bromine compound.....	37.0%
Sheep cephalin (1) 0.3353 g. bromine compound.....	34.5%
Beef cephalin (4) 0.3047 g. bromine compound.....	34.5%

The lowness of a few of the values can easily be accounted for by supposing that a small amount of stearic acid was present. That would

be the case if the lead separation had not been complete, and of that it is difficult to be certain.

In order to be sure that this method of determining the bromine content of a fatty acid derivative was entirely correct, the amount of bromine in pure dibromostearic acid, tetrabromostearic acid and hexabromostearic acid was found.

	G.	Obtained. Br.	Theoretical. Br.
Pure dibromostearic acid.....	0.2941	35.9%	36.2%
Pure tetrabromostearic acid.....	0.2134	53.2%	53.3%
Pure hexabromostearic acid.....	0.1070	62.8%	63.3%

It will be noticed that these values agree as well as could be expected with the theoretical bromine values.

The identity of the oleic acid was more firmly established by oxidizing a mixture of the fatty acids of cephalin in the usual way with a permanganate solution. A hydroxy derivative was found that had the properties of dihydroxy stearic acid. It was insoluble in water, somewhat soluble in ether, and readily soluble in hot alcohol.

**Cephalinic Acid.**—The petroleum-ether-insoluble fraction was purified by dissolving it in ether and filtering to remove any hexa or octa bromine derivatives. The ether solution was evaporated to dryness and the residue recrystallized from petroleum ether.

From the work done on this bromine derivative it is difficult to say what the formula of the compound really is. The bromine values found can be interpreted in several ways.

	Br.
Sheep cephalin (8) 0.2214 g. bromine compound.....	61.4%
Sheep cephalin (4) 0.2112 g. bromine compound.....	59.8%
Sheep cephalin (4) 0.2115 g. bromine compound.....	60.5%
Beef cephalin (4) 0.1178 g. bromine compound.....	59.0%

Though the bromine derivative from the best samples of cephalin gave about 60% of bromine, a few were as low as 56%. Probably the best way to explain low values in the petroleum-ether-insoluble fraction is by reasoning that any of the partially oxidized fatty acids, when brominated and separated as above described, would go into this fraction. It is extremely difficult to be sure that the product has been freed from such oxybromo acids. They would lower the bromine value. It is almost impossible, even with the precautions adopted against oxidation in this investigation, to say with certainty that no unsaturated bonds in the fatty acids had been saturated with oxygen. The principle evidence of oxidation in the cephalin was a darkening in color. Cephalin (4) and (8) were about white; a faint yellowish color was evident when a compact mass was observed. The amount of oxidation was very small, at most.

It is probably not a hexabromobehenic or lignoceric acid, because one

would expect these derivatives to have melting points about  $180^{\circ}$  whereas the best samples of cephalinic bromide melted at about  $120^{\circ}$ . The bromides of the higher acids would undoubtedly be even less soluble in ether than hexabromostearic acid, but the bromide of cephalinic acid is soluble in ether, though not so readily soluble as the tetrabromostearic acid. Besides, the melting point is too high for the tetrabromo compound. There seems to be no tendency, even at high temperatures, to form the soluble linolic bromide. The appearance of cephalinic bromide is also different from linolic bromide. The former crystallizes out of ether, slowly but continuously as the ether evaporates, in rather heavy plates, while the latter does not crystallize till the ether solution is concentrated, and then it separates as needles or as a semisolid mass containing the liquid as well as solid tetrabromide. The characteristics of the cephalinic bromide agree best with Thudicum's<sup>1</sup> data on the barium salt. From his results cephalinic acid would be probably an hydroxypalmitic or stearic acid with four unsaturated bonds in it. The data in this paper agree fairly well with a tetrabromo hydroxypalmitic acid.

#### Clupanodonic Acid.

The ether-insoluble bromine fraction gave bromine values ranging from 67% to 69.4%. Several analyses on the best cephalin preparations follow:

	Br.
Beef cephalin (4) 0.0827 g. bromine compound.....	67.7%
Sheep cephalin (4) 0.2144 g. bromine compound.....	69.4%
Sheep cephalin (8) 0.1967 g. bromine compound.....	68.8%
Sheep cephalin (4) 0.2260 g. bromine compound.....	68.7%

The theoretical percentage of bromine in octobromostearic acid is 69.6. The above values agree as well as one could expect, considering the possibilities of slight oxidation during the preparation and hydrolysis of the cephalin. However, the difference in amount of bromine in  $C_{18}H_{28}O_2Br_8$  and  $C_{20}H_{32}O_2Br_8$  is but 2%. There is some evidence for believing that the latter compound is one of the bromination products of liver lecithin. It is entirely possible, then, that the ether-insoluble bromo compound is not a derivative of clupanodonic acid but of the next higher homolog. The values more nearly agree with clupanodonic acid, however.

This difficulty was not solved by melting-point determinations on the bromo compound. When heated rather rapidly it darkens at  $220^{\circ}$  but does not melt. Because of the uncertainty of this darkening point it is not a reliable way of differentiating between the two homologs. Probably both darken between  $210^{\circ}$  and  $220^{\circ}$  when the temperature is rapidly raised to that point.

<sup>1</sup> Thudicum, "Die chemische Constitution des Gehirns," p. 149 (1901).

**General Statements.**—From the data presented it is reasonably certain that the two fatty acids in largest amounts in cephalin are stearic and oleic.

The evidence for clupanodonic acid is rather conclusive though not entirely so. Other methods besides the bromination one are being tried to clear up this point.

The greatest uncertainty centers around cephalinic acid. The solubilities and appearance of the bromo derivative strongly suggest linolic acid, but the bromine value is too high. The melting point and percentage of bromine indicate an impure linolenic acid or a higher homolog. Several lines of attack are being carried on the more clearly to understand this acid.

### Summary.

1. Somewhat more than one-fourth of the acids of cephalin is in the form of stearic, more than one-half oleic, one-tenth cephalinic, and one-twentieth clupanodonic.

2. From the varying amount of these acids present it is concluded that they are present in mixed cephalins, these various cephalins being closely associated.

3. There is no marked difference, either, in the kind or amount of acids in sheep and beef brain cephalins.

4. The evidence presented strongly indicates ordinary stearic and oleic acids as the principal fatty acids of cephalin.

5. The evidence for the identity of clupanodonic and cephalinic acids is not conclusive.

LOS ANGELES, CAL.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY.]

## THE ACTION OF ANHYDROUS ALUMINIUM CHLORIDE UPON UNSATURATED COMPOUNDS.

BY W. E. HENDERSON AND WILMER C. GANGLOFF.

Received May 10, 1916.

It is known that the product obtained by cracking petroleums with aluminium chloride under certain conditions consists very largely of saturated hydrocarbons; whereas distillation under pressure results in a large percentage of unsaturated compounds. One possible explanation of this peculiarity is that the aluminium chloride combines with any unsaturated hydrocarbons formed in the reaction and holds them back from the distillate. The simple experiment of shaking ordinary gasoline with the anhydrous chloride showed that by this treatment all of the unsaturated hydrocarbons are converted into a dark-colored sludge, and that the gasoline resulting gives no color with concentrated sulfuric acid. Petroleum ether acts in a similar way.

A careful review of the literature discloses the fact that very little work

is recorded upon the action of anhydrous aluminium chloride with unsaturated hydrocarbons. This is somewhat surprising in view of the large number of researches upon the addition products that the reagent forms with so many diverse types of organic compounds, and the rôle it plays in the Friedel-Crafts reaction. The chief researches bearing directly upon the subject are cited in the foot-note.<sup>1</sup> From this work it appears that various complex and ill-defined products have been described as resulting from passing vapors of unsaturated hydrocarbons over aluminium chloride heated to various temperatures; that solutions of aluminium chloride in organic solvents absorb such vapors; and that no well-defined products suitable for analysis have been obtained from these solutions.

We have undertaken a study of this field, and have secured a number of positive results. Inasmuch as it will be some time before the experiments now planned can be completed, it is thought best to publish a brief report upon the results already obtained.

**The Action of Acetylene upon Anhydrous Aluminium Chloride.**—Baud states that pure dry acetylene is completely absorbed by anhydrous aluminium chloride in a closed vessel, even in the cold. If heated to 70° the absorption is complete in a few minutes. A different reaction takes place when a current of acetylene is passed over the hot chloride, a reddish black sublimate forming which finally becomes black. The gas is almost all absorbed, and there is a considerable evolution of heat. At 120–130°, with a continuation of the gaseous current there is no further increase in the weight of the sublimate. To the products formed Baud assigns the formulas  $(C_{20}H_{16})_{7.}Al_2Cl_6$  and  $(C_{10}H_{16})_{7.}Al_2Cl_6$ .

We repeated this work, generating the acetylene from calcium carbide and passing the dried gas into a closed vessel containing finely powdered, freshly prepared, anhydrous aluminium chloride. No noticeable absorption occurred within several hours. Upon heating the aluminium chloride at 60–62° a reddish brown sublimate appeared, dense vapors were produced, and the sublimate soon turned black and remained unchanged after heating to 140°. Heating to 240° yielded nothing but tar. The black substance resembled pitch, and under the microscope showed no crystalline form. It was evidently a complex mixture.

**The Action of Acetylene upon Alcoholic Solutions of Aluminium Chloride.**—Dry acetylene prepared from calcium carbide was passed into a solution of aluminium chloride in absolute alcohol, and after thorough

<sup>1</sup> Friedel and Crafts, *Compt. rend.*, 84, 1392 (1877); *Ann. chim. phys.*, [6] 1, 440, 446, 449, 461, 510, 518 (1884); Adrianowsky, *Ber.*, 12, 853 (1879); Gustavson, *J. prakt. Chem.*, [2] 42, 501 (1890); Winogradoff, *Ibid.*, 37, 110 (1888); Baud, *Chem. News*, 81, 286 (1900); Perrier, *Compt. rend.*, 122, 196 (1896); *Ber.*, 33, 815 (1900); Menschutkin, *J. Russ. Phys. Chem. Soc.*, 42, 1310 (1910); Steele, *J. Chem. Soc.*, 83, 1470 (1903).

saturation for several hours the solution was set aside in a desiccator charged with acetylene. After five days small, colorless, glistening, well-formed crystals appeared. These were very soluble, hygroscopic, difficult to dry, soluble in most solvents, and they decomposed with great ease. Experiments showed that this product was not merely aluminium chloride with alcohol of crystallization. When treated with acids the crystals evolved acetylene, as was shown by the precipitation of copper acetylide from ammoniacal cuprous chloride. Many difficulties were encountered in the analysis of this and similar products. The compound loses acetylene and hydrogen chloride on standing, and in the process of drying. It is exceedingly difficult to burn the carbon by ordinary combustion methods and wet methods were resorted to. Possibly aluminium carbide is formed when the compound is heated, rendering combustion difficult. The analysis, while leaving much to be desired, rather clearly indicates the composition of the product.

Calc. for  $\text{AlCl}_3 \cdot 2\text{C}_2\text{H}_2 \cdot 2\text{H}_2\text{O}$ : Al, 12.23; Cl, 48.03; C, 21.67; H, 3.61. Found: Al, 12.47; Cl, 45.59; C, 25.70; H, 3.97.

The presence of water in the alcohol prevents the formation of any crystalline product.

**The Action of Ethylene upon Aluminium Chloride.**—The action of ethylene upon aluminium chloride has been found to be closely parallel to that of acetylene. Ethylene was prepared from ethyl alcohol and sulfuric acid at  $170^\circ$ , dried in a train of sulfuric acid and potassium hydroxide, and passed into a closed vessel containing anhydrous aluminium chloride. No noticeable absorption occurred during several hours. Upon heating, a black tarry mass was formed containing much free carbon, and no crystalline product was obtained. A solution of aluminium chloride in absolute alcohol was then saturated with ethylene, and was allowed to stand for a week in a desiccator. A well-crystallized product was obtained closely resembling the product formed with acetylene. It was very hygroscopic, lost ethylene and hydrogen chloride in drying, and decomposed with great ease. The analysis for carbon presented the same difficulties as in the case described.

Calc. for  $\text{AlCl}_3 \cdot 3\text{C}_2\text{H}_4 \cdot \text{H}_2\text{O}$ : Al, 11.58; Cl, 45.15; C, 30.56; H, 5.99. Found: Al, 12.61; Cl, 44.76; C, 30.49; H, 6.45.

In addition to those described, crystalline products have been obtained with propylene, butylene, styrolene, oleic acid, and amylene. While well-crystallized, these bodies are very soluble, are difficult to crystallize, have a considerable dissociation pressure, and are, in general, very difficult to prepare for analysis. We are not at present prepared to suggest formulas for them, but shall hope to make a more complete report at some future time.

[CONTRIBUTIONS FROM THE SHEFFIELD CHEMICAL LABORATORY OF YALE UNIVERSITY.]

**RESEARCHES ON PYRIMIDINES. LXXVIII. THE REDUCTION OF 2-MERCAPTO-6-CHLOROPYRIMIDINES.**

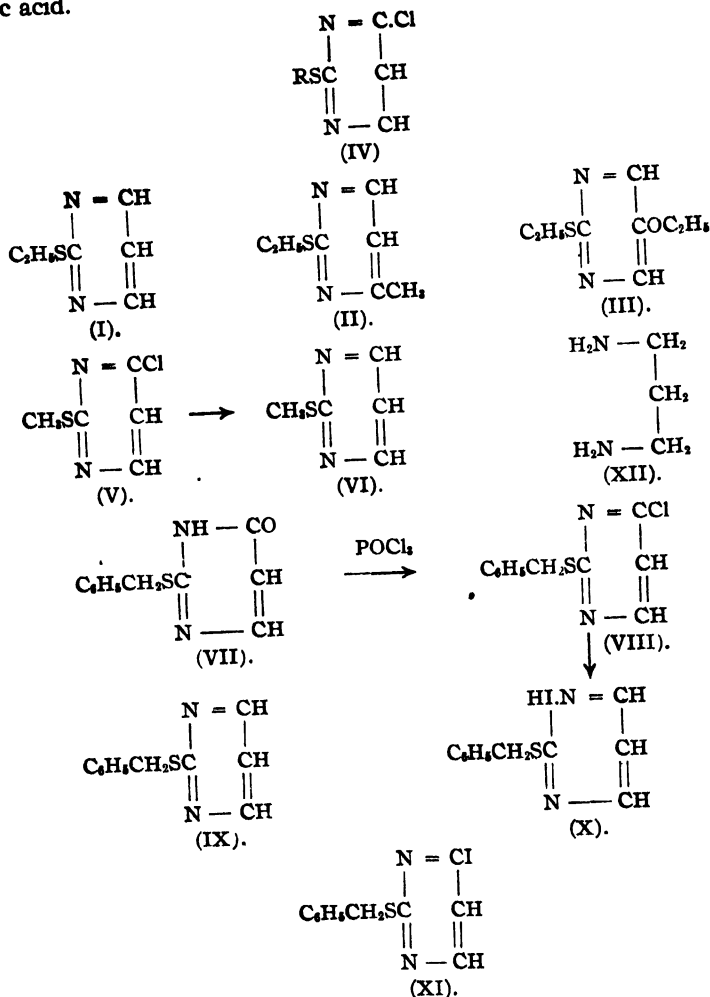
BY TREAT B. JOHNSON AND A. WILLARD JOYCE.

Received May 20, 1916.

In a previous paper from this laboratory Johnson and Joyce<sup>1</sup> have shown that 2-mercapto-6-chloropyrimidines (IV) can be reduced easily by the action of zinc dust with formation of the corresponding 2-mercaptopyrimidines. They prepared in this manner 2-ethylmercaptopyrimidine (I), 2-ethylmercapto-4-methylpyrimidine (II) and 2-ethylmercapto-5-ethoxypyrimidine (III). These are the only representatives known of this new class of mercaptopyrimidines. Such combinations can now be prepared easily in quantity by application of our method. In no case have we failed, thus far, to bring about a smooth reduction when we employed pyrimidine combinations containing methyl- and ethylmercapto groups in the 2-position of the pyrimidine ring. 2-Methylmercapto-6-chloropyrimidine (V) has been prepared<sup>2</sup> and we find that this undergoes reduction as smoothly as its corresponding 2-ethylmercapto compound. The yield of the reduced pyrimidine (VI), in this case, was 70% of the theoretical. A chlorine atom in position 2 also does not hinder the reduction of a halogen in the 6-position as 2,6-dichloro-5-ethoxypyrimidine is readily reduced by zinc dust to the corresponding 2-chloro-5-ethoxypyrimidine.<sup>3</sup> We have now introduced a benzylmercapto grouping into position 2, and have prepared the hitherto unknown 2-benzylmercapto-6-chloropyrimidine (VIII). The latter was easily obtained by the action of phosphorus oxychloride on 2-benzylmercapto-6-oxypyrimidine<sup>4</sup> (VII). All attempts to reduce this pyrimidine to the corresponding 2-benzylmercaptopyrimidine (IX) have so far been unsuccessful. Not only was it found to be extremely stable in the presence of zinc dust, but it was also not reduced by sodium-amalgam and zinc-amalgam. We also investigated its behavior towards hydriodic acid and found that here also the pyrimidine exhibited great stability. Owing to its weak basic properties it simply combined with hydriodic acid forming a characteristic, crystalline salt (X). This ability to form salts is a property of these mercaptochloropyrimidines which hitherto has not been emphasized by us. On warming with hydriodic acid such combinations are decomposed with evolution of mercaptans. The hydriodide of this base (X) is easily decomposed by water with dissociation into the free pyrimidine and hydriodic acid. There was no evidence of an exchange of halogens

<sup>1</sup> THIS JOURNAL, 37, 2151 (1915).<sup>2</sup> Wheeler and Bristol, *Am. Chem. J.*, 33, 437 (1905).<sup>3</sup> Johnson and Joyce, *Loc. cit.*<sup>4</sup> Wheeler and Liddle, *Am. Chem. J.*, 40, 554 (1908).

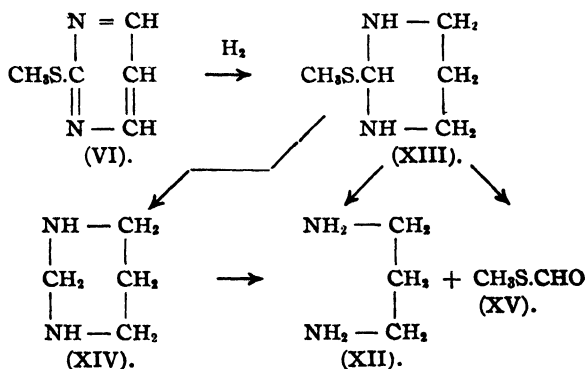
with production of 2-benzylmercapto-6-iodopyrimidine (XI) and hydrochloric acid.



While bases of the type of 2-methylmercaptopyrimidine (VI) resist further reduction by the action of zinc dust, on the other hand, when subjected to the action of metallic sodium in alcoholic solution they undergo characteristic changes. Not only is the ring completely saturated with hydrogen, but the pyrimidine cycle is finally ruptured and an aliphatic diamine is formed. 2-Methylmercaptopyrimidine; for example, is reduced under such conditions with production of trimethylenediamine (XII) and methylmercaptan. The yield of the diamine was equivalent to 60 per cent. of a theoretical yield showing that we have here a prac-

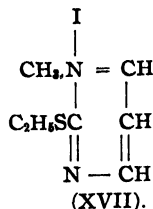
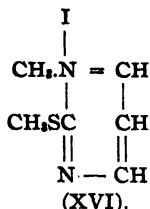


tical method of synthesizing aliphatic combinations of this type. Regarding the mechanism of this reaction it seems probable that the first phase of the transformation involves a complete reduction of the pyrimidine (VI), with formation of its hexahydro derivative represented by Formula XIII. This then might break down theoretically in two ways, namely, either undergo further reduction in the alkaline solution to mercaptan and the sulfur-free pyrimidine (XIV), which on hydrolysis would give formaldehyde and the diamine (XII), or the pyrimidine (XIII) undergo hydrolysis directly with production of the diamine (XII) and methylthiolformate (XV). The latter would then be saponified by the alkali present giving formic acid and methylmercaptan. Mercaptan was always recognized by its odor, but the formation of formaldehyde of formic acid was not established. The reaction may be expressed as follows:



An increase in the basicity of the pyrimidine molecule is brought about by the transformation of a 2-mercapto-6-oxypyrimidine into a 2-mercapto-6-chloropyrimidine and a 2-mercaptopyrimidine. The oxygen pyrimidines are extremely weak bases<sup>1</sup> and possess acid properties on account of the presence of a CO-NH grouping in their molecules. The mercaptochloropyrimidines and corresponding 2-mercaptopyrimidines, on the other hand, are insoluble in alkaline solutions. They do not contain any ionizable hydrogen and interact with acids with formation of salts. The latter are, however, unstable and easily undergo dissociation in aqueous solution. The 2-mercaptopyrimidines are also characterized by their property of forming addition products with alkyl halides. Two combinations of this type have been prepared and are represented by Formulas XVI and XVII. Both were obtained in a crystalline condition and could be crystallized from alcohol without decomposition. So far as we are aware, the corresponding 2-mercapto-6-oxypyrimidines have not been shown to form analogous

<sup>1</sup> Wheeler and Bristol, *Loc. cit.*



addition combinations with alkyl halides. The investigation of the behavior of pyrimidine compounds towards reducing agents will be continued.

### Experimental Part.

**Reduction of 2-Methylmercapto-6-chloropyrimidine with Zinc Dust. The Formation of 2-Methylmercaptopyrimidine (VI).**—The 2-methylmercapto-6-chloropyrimidine, which was used in this work, was prepared according to the method of Wheeler and Bristol<sup>1</sup> by the action of phosphorus oxychloride on 2-methylmercapto-6-oxypyrimidine. In order to obtain the best yields of the reduced pyrimidine, it was found advisable, by experience, to work with small quantities of the chloropyrimidine at a time. Our procedure was as follows: Eighty grams of the chloropyrimidine were divided into four portions and 20 grams placed in separate flasks with 40 grams of zinc dust, 100 cc. of water and 100 cc. of alcohol. These mixtures were then boiled for one-half an hour, when the excess of zinc dust was filtered off and the alcoholic filtrates combined, and then concentrated under diminished pressure. A dark-colored oil was obtained, which was extracted with ether and dried over calcium chloride. A small amount of 2-methylmercapto-6-oxypyrimidine was identified here and was formed by partial hydrolysis of the 2-methylmercapto-6-chloropyrimidine during the reduction. After removing the ether, the oil was purified by distillation under diminished pressure and boiled at 99–100° at 14 mm. pressure. This was a colorless liquid having an odor similar to that of pyridine and quinoline. On exposure to the air the pyrimidine gradually turns light brown, but this change does not take place as readily as in the case of the corresponding 2-ethylmercaptopyrimidine previously described by Johnson and Joyce.<sup>1</sup> The yield is about 70% of the theoretical. This pyrimidine, as well as the 2-ethylmercaptopyrimidine, forms salts with strong acids, the hydrochloride dissolving in water without dissociation. One part of the base dissolves in about 20 parts of cold water. This aqueous solution does not give an alkaline reaction with litmus or turmeric paper. The pyrimidine is volatile with steam. Analysis:

Calc. for  $\text{C}_5\text{H}_6\text{N}_2\text{S}$ : N, 22.22. Found: N, 22.19, 22.02.

Index of refraction:  $n_D$  at 20° = 1.5856 (Abbe). Index of refraction of 2-ethylmercaptopyrimidine:  $n_D$  at 20° = 1.5673 (Abbe).

<sup>1</sup> *Loc. cit.*

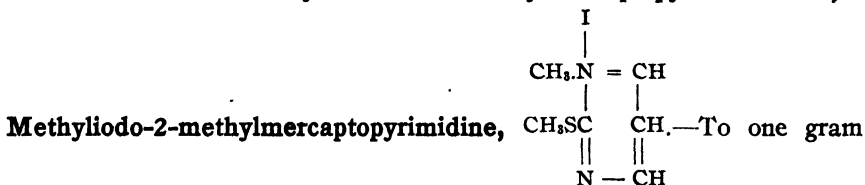
**Hydrochloride.**—This salt was prepared by passing dry hydrochloric acid gas into an ethereal solution of the pyrimidine. It crystallized in needles which melted at  $147^{\circ}$ . Analysis:

Calc. for  $C_5H_6N_2S.HCl$ : N, 17.23. Found: N, 17.1, 17.00.

**Hydrobromide.**—This was prepared by mixing strong hydrobromic acid solution with the mercaptopyrimidine. They interacted immediately with formation of a crystalline salt. This was purified by crystallization from absolute alcohol and separated in the form of rectangular prisms melting at  $187^{\circ}$ . Analysis:

Calc. for  $C_5H_6N_2S.HBr$ : N, 13.52. Found: N, 13.2, 13.31.

**The Addition of Methyl iodide to 2-Methylmercaptopyrimidine. 1,1-**



of the pyrimidine were added 2 grams of methyl iodide and the mixture allowed to stand at room temperature overnight. When examined the next morning the mixture had solidified to a crystalline mass of needles. These were triturated with cold ether and crystallized from boiling absolute alcohol. The pyrimidine separated, on cooling, in the form of irregular, prismatic rods or needles. They melted at  $146\text{--}147^{\circ}$  to a red oil. This addition product is very soluble in water. Concentrated sulfuric acid interacted with it with liberation of iodine and when the compound was treated with dilute alkali methylmercaptan was slowly evolved.

Calc. for  $C_6H_8N_2SI$ : N, 10.44. Found: N, 10.11, 10.36.

**1,1-Methylido-2-ethylmercaptopyrimidine.**—This pyrimidine was prepared in a manner similar to that employed for the preparation of the preceding addition product. It crystallized from absolute alcohol in needles which melted at  $135^{\circ}$  to a red oil. Analysis:

Calc. for  $C_8H_{11}N_2SI$ : N, 9.52. Found: N, 9.36.

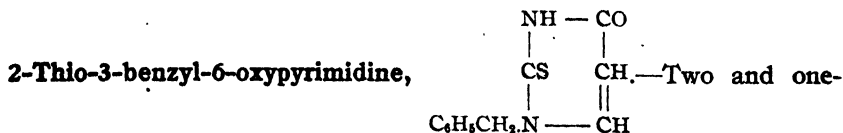
**The Formation of Trimethylenediamine by Reduction of 2-Ethylmercaptopyrimidine.**—This mercaptopyrimidine is easily converted into trimethylenediamine by reduction with sodium and alcohol. The procedure was as follows: Ten grams of the 2-ethylmercaptopyrimidine were dissolved in 150 cc. of absolute alcohol and this solution then added slowly upon 20 grams of metallic sodium (2 molecular proportions). As the reduction proceeded the alcoholic solution assumed a dark red color and ethylmercaptan and ammonia were evolved. For complete solution of the sodium 100 cc. more of alcohol were finally added and the solution finally heated on the steam bath. After complete solution of the sodium,

air was blown through the mixture to expel as much ammonia as possible and the solution then subjected to steam distillation. The distillate containing alcohol and base were conducted into hydrochloric acid. After complete distillation the hydrochloric acid solution was evaporated to dryness, *in vacuo*, and the hydrochloride of trimethylenediamine purified by crystallization from 25% alcohol. In this manner it was easily separated from ammonium chloride. The salt crystallized in beautiful transparent prisms which melted at 242–243°. This same melting point is also to be assigned to the compound prepared by Fischer's<sup>1</sup> method. A mixture of the salt prepared by both methods melted at 242–243°. The yield of hydrochloride was 6.2 grams or 60% of the theoretical. Analysis:

Calc. for  $C_6H_{10}N_2 \cdot 2HCl$ : N, 19.04. Found: N, 19.00, 19.02.

**Alkylation of 2-Thiouracil with Benzylchloride. The Formation of 2-Benzylmercapto-6-oxypyrimidine (IX) and 2-Benzylmercapto-3-benzyl-6-oxypyrimidine.**—2-Benzylmercapto-6-oxypyrimidine has been described by Wheeler and Liddle,<sup>2</sup> and was prepared for our work according to their directions. We made the observation, however, that this is not the only product formed by allylation with benzyl chloride. We succeeded in isolating another derivative in small quantity, which crystallized from alcohol in colorless, flat prisms melting at 144–145° to a clear oil. The yield of this pyrimidine was about 5–10% of the theoretical and it was identified as 2-benzylmercapto-3-benzyl-6-oxypyrimidine. It was very soluble in alcohol and ether, and insoluble in water, aqueous alkali and acid solutions. Analysis:

Calc. for  $C_{18}H_{18}ON_2S$ : N, 9.09. Found: N, 8.8.



half grams of the above 2-benzylmercaptopyrimidine were dissolved in 100 cc. of concentrated hydrochloric acid, by warming on the steam bath, and the solution then evaporated to dryness. The residue was crystallized from boiling alcohol. On cooling, this thiopyrimidine separated in the form of plates, which melted at 231°. These gave a strong test for sulfur. Analysis:

Calc. for  $C_{11}H_{10}ON_2S$ : N, 12.84. Found: N, 13.00.

**Desulfurization of 2-Thio-3-benzyl-6-oxypyrimidine with Formation of 2,6-Dioxy-3-benzylpyrimidine.**<sup>3</sup>—One and two-tenths grams of the thiopyrimidine were digested for seven hours with 4 grams of chloro-

<sup>1</sup> *Ber.*, 17, 1799 (1884).

<sup>2</sup> *Am. Chem. J.*, 40, 554 (1908).

<sup>3</sup> Johnson and Derby, *Am. Chem. J.*, 40, 444 (1908).

acetic acid. The pyrimidine dissolved completely and, on cooling, the desulfurized pyrimidine separated in a crystalline condition. It crystallized from alcohol in prisms melting at  $173-174^{\circ}$  as originally observed by Johnson and Derby. A mixture of our pyrimidine and the isomeric 1-benzyl-2,6-dioxypyrimidine melted at  $140-155^{\circ}$ .

**2-Benzylmercapto-6-chloropyrimidine.**—Forty-four grams of the 2-benzylmercapto-6-oxypyrimidine were mixed with 25 cc. of phosphorus oxychloride in a distilling flask and the mixture then heated in an oil bath for about 5.5 hours. The pyrimidine dissolved completely and hydrogen chloride was evolved. The excess of phosphorus oxychloride was then removed by distillation, under diminished pressure at  $100^{\circ}$ , and the thick, viscous oil remaining behind poured upon crushed ice to destroy the last traces of phosphorus halide. After extraction with ether and drying over calcium chloride the oil was then distilled under diminished pressure. It boiled at  $210^{\circ}$  at 18 mm. On cooling, this oil solidified in the form of long prisms which melted at  $48-49^{\circ}$ . The yield was 33 grams or 70% of the theoretical. Analysis:

Calc. for  $C_{11}H_9N_2SCl$ : N, 11.84. Found: N, 11.71, 11.86.

This pyrimidine is soluble in ether, alcohol and benzene. It is insoluble in water, dilute acid and alkaline solutions and is hydrolyzed by digestion with strong hydrochloric acid with formation of uracil.

**Attempts to Reduce 2-Benzylmercapto-6-chloropyrimidine: Action of Zinc Dust.**—Five grams of the chloropyrimidine were dissolved in a mixture of 100 cc. of alcohol and 50 cc. of water, and 15 grams of zinc dust added. After boiling for 5 hours the excess of zinc was separated by filtration and the alcohol removed by evaporation under diminished pressure. The oil remaining behind was then extracted with ether and dried over calcium chloride. On evaporating the ether, unaltered 2-benzylmercapto-6-chloropyrimidine separated in the form of needles and melted at  $45-47^{\circ}$ .

**Action of Zinc Amalgam.**—Five grams of the chloropyrimidine were dissolved in a mixture of equal volumes of water and alcohol (150 cc.) and 20 grams of amalgamated zinc suspended in the solution. This was then boiled for 4 hours and the zinc separated by filtration. On evaporating the alcohol and water under diminished pressure, we obtained an oil which finally solidified and was identified as the unaltered chloride. The same result was obtained when an attempt was made to reduce the chloropyrimidine with sodium amalgam.

**The Action of Hydriodic Acid.**—Nine grams of 2-benzylmercapto-6-chloropyrimidine were melted in a flask and 15 cc. of colorless hydriodic acid (b. p.  $127^{\circ}$ ) added. There was an immediate reaction with evolution of heat and formation of a crystalline product. The entire mixture became solid. The odor of benzyliodide was also noticeable, indicating

a partial hydrolysis of the pyrimidine. The crystals, which were yellow, were filtered off, washed with ether and dried in a vacuum over sulfuric acid. They melted at  $136^{\circ}$ . A nitrogen determination showed that we were dealing with a hydriodic acid salt of the chloropyrimidine. The compound also gave tests for chlorine and iodine.

Calc. for  $C_{11}H_8N_2SCl.HI$ : N, 7.68. Found: N, 7.3, 7.26.

This salt could not be crystallized from the common solvents without dissociation. It is insoluble in ether, carbon tetrachloride and benzene, slightly soluble in acetone and very soluble in absolute alcohol. It was easily hydrolyzed by water, giving an oil which finally solidified and melted without further purification at  $45^{\circ}$ . This was identified as the original chloropyrimidine. When this was mixed with some of the chloro compound there was no lowering of the melting point. The yield of the salt was 12 grams of 84% of the theoretical.

NEW HAVEN, CONN.

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[CONTRIBUTIONS FROM THE SHEFFIELD CHEMICAL LABORATORY OF YALE UNIVERSITY.]  
**STUDIES ON NITRATED PROTEINS. V. THE HYDROLYSIS OF  
NITRO-FIBROIN WITH HYDROCHLORIC ACID.**

By TREAT B. JOHNSON AND ARTHUR J. HILL.

Received May 20, 1916.

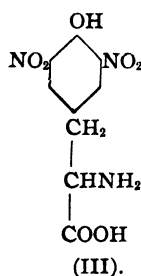
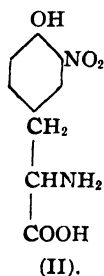
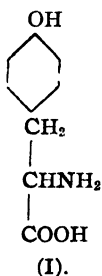
The term "Nitro-Fibroin," as we shall apply it in this paper, is the name of a modified protein which is obtained by treatment of pure fibroin, under definite conditions, with nitric acid of specific gravity 1.12. This sulfur-free protein is very easily attacked by strong nitric acid, but the reaction is not productive of consistent results unless applied under carefully regulated conditions. We have found that, if the protein be exposed to the action of acid of the above strength for a long time and at ordinary temperature ( $18-25^{\circ}$ ), a stage in the transformation is finally reached where practically no further action on the protein takes place. In other words, it has been our experience that a nitrated protein of quite definite constitution is formed, which is optically active and does not respond to Millon's test for tyrosine. This substance is obtained in the form of an orange-colored powder and the yield corresponds to about 70% of the weight of the original protein. The method of preparing this interesting product (nitro-fibroin) has already been described in a previous paper from this laboratory.<sup>1</sup>

Inouye<sup>2</sup> prepared a nitrated fibroin by the action of cold nitric acid (sp. gr. 1.12) on silk fibroin and obtained after 48 hours' treatment a yield of nitroprotein corresponding to 85-90% of the weight of fibroin taken. This product was subjected to hydrolysis with dilute sulfuric

<sup>1</sup> Johnson, Hill and O'Hara, *THIS JOURNAL*, 37, 2170 (1915).

<sup>2</sup> *Z. physiol. Chem.*, 81, 80 (1912).

acid, when he made the interesting observation that a nitrotyrosine of unknown constitution was one of the products of decomposition. Johnson<sup>1</sup> repeated this work of Inouye's and isolated, after hydrolysis, the same nitroamino acid. He showed that it is a definite combination formed by the action of nitric acid on the tyrosine in the protein and is to be represented structurally as an *o*-nitro derivative of this  $\alpha$ -amino acid as represented by Formula II.<sup>2</sup>



In our third paper on nitrated proteins<sup>3</sup> we called attention to the interesting observation that the nitration reaction—fibroin + nitric acid—can be followed qualitatively by Millon's test for only a few hours. Generally, after about 24 hours' treatment at ordinary temperature, the protein fails to respond to this characteristic reaction, indicating a fundamental change in the tyrosine phenol nucleus, and possibly the end of the first phase of the reaction. The isolation of *o*-nitrotyrosine (II) from the products of hydrolysis of Inouye's nitrated fibroin was the first definite evidence produced showing the true nature of this change. Neither Inouye nor Johnson obtained any evidence of the presence of a dinitrotyrosine (III) among the hydrolytic products of this nitrated protein.

In the light of these results it was therefore of especial interest to investigate the character of the hydrolytic products formed by complete hydrolysis of "nitro-fibroin" prepared according to the method of Johnson, Hill and O'Hara.<sup>4</sup> It was important to determine whether the tyrosine in fibroin undergoes further changes by long exposure to nitric acid (sp. gr. 1.12) with formation of 3,5-dinitrotyrosine (III), which has recently been described by Johnson and Kohmann.<sup>5</sup> Furthermore, it was also important to determine the nature of the other  $\alpha$ -amino acids which are constituents of nitro-fibroin. The complete hydrolysis of this protein has now been accomplished, and in this paper we record the results of our investigation.

<sup>1</sup> THIS JOURNAL, 37, 2598 (1915).

<sup>2</sup> Johnson and Kohmann, THIS JOURNAL, 37, 1863 (1915).

<sup>3</sup> Johnson, Hill and O'Hara, *Loc. cit.*

<sup>4</sup> *Loc. cit.*

<sup>5</sup> THIS JOURNAL, 37, 2164 (1915).

### Experimental.

**The Preparation of Nitro-Fibroin in Quantity.**—The nitro-fibroin was prepared according to directions already given in the literature,<sup>1</sup> but we worked with much larger quantities than were used in our original investigation. In applying the reaction on a large scale, it is interesting to note that we again confirmed our original observation, namely, that the nitration of fibroin under the conditions described was productive of a remarkably constant amount of nitro-fibroin. From 479 g. of fibroin, dried at 100°, we obtained 345 g. of the nitrated protein or about 72% of the weight of the original silk fibroin. This result is in close agreement with those recorded in our previous paper. In other words, this yield calculated upon the basis of 20 g. of fibroin gives the figure 14.40, while in our original work we actually obtained in two experiments 14.26 and 14.20 g. of the nitro-fibroin from 20 g. of fibroin. This experiment was repeated with the same result. The nitric acid filtrates left after filtration of nitro-fibroin were saved (see below).

**Hydrolysis with Hydrochloric Acid.**—Our method of hydrolyzing nitro-fibroin was as follows: Three hundred grams of the nitrated protein, corresponding to 416.5 g. of silk fibroin, were dissolved in 1200 cc. of hydrochloric acid (sp. gr. 1.19). Solution was brought about very quickly and was attended with some foaming, but there was no evolution of carbon dioxide. This solution was then digested in an oil bath for 15 hours at a temperature of 120–130°. It was then allowed to stand at ordinary temperature for 3 days when a dense, brownish precipitate was observed to have deposited in the acid solution. The yield of this material was increased by concentration of the acid solution and then saturating the same at 0° with hydrochloric acid gas. After repeating this operation several times the precipitates were combined and decolorized by digestion in strong hydrochloric acid with animal charcoal. The material was then purified by recrystallization from the same solvent. We obtained in this manner 20 g. of pure material. This substance crystallized from hydrochloric acid in the form of characteristic yellow needles which melted with effervescence at 237°. This compound contained chlorine and proved to be identical with the hydrochloride of 3-nitrotyrosine (II) previously synthesized by Johnson and Kohmann<sup>2</sup> and also isolated by Johnson<sup>2</sup> from the products resulting from the hydrolysis of Inouye's nitrated protein with sulfuric acid.

Calc. for  $C_9H_{11}O_4N_2Cl$ : N, 10.70; Cl, 13.51. Found: N, 10.85, 10.95; Cl, 13.61.

The identity of this salt was also established by the fact that it underwent decomposition with alkali giving 3-nitrotyrosine II melting at 237°

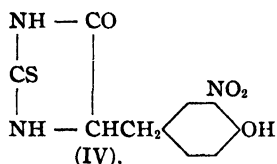
<sup>1</sup> Johnson, Hill and O'Hara, *Loc. cit.*

<sup>2</sup> *Loc. cit.*



with effervescence. A mixture of our hydrolytic product and the synthetic 3-nitrotyrosine melted at 237°.

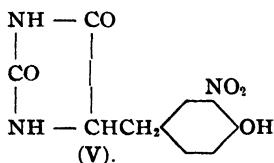
Our nitrotyrosine also interacted smoothly with ammonium thiocyanate in acetic anhydride solution giving 2-thio-4(3-nitro-4-hydroxybenzyl)-hydantoin (IV)



which has already been described by Johnson and Kohmann.<sup>1</sup> It melted at 238–240° with decomposition.

Calc. for  $\text{C}_{10}\text{H}_9\text{O}_4\text{N}_3\text{S}$ : N, 15.74. Found: N, 15.65.

When this 2-thiohydantoin (IV) is desulfurized with chloroacetic acid it is transformed into 4-(3-nitro-4-hydroxybenzyl)-hydantoin (V).<sup>2</sup> We applied the same reaction with our 2-thiohydantoin and obtained the same sulfur free hydantoin. It melted at 224° to a clear oil. We also obtained the same hydantoin (V) by the action of potassium cyanate on the hydrochloride of our 3-nitrotyrosine from nitro-fibroin. Two



grams of the hydrochloride of 3-nitrotyrosine were dissolved in water with 2 g. of potassium cyanate and the solution evaporated to dryness. The residue was then triturated with 15 cc. of concentrated hydrochloric acid and again evaporated to dryness. In this manner we obtained smoothly the hydantoin (V) which crystallized from hot water or glacial acetic acid in the form of rosetts of needles. They melted at 224° to a clear oil. A mixture of this product and the synthetic hydantoin melted at exactly the same temperature.

Calc. for  $\text{C}_{10}\text{H}_9\text{O}_5\text{N}_3$ : N, 16.75. Found: N, 16.62.

It is interesting to note here that during all these operations we obtained no evidence of changes indicating the presence of any 2-nitrotyrosine or 3,5-dinitrotyrosine. The dinitrotyrosine exhibits a behavior similar to that of 3-nitrotyrosine, when dissolved in strong hydrochloric acid, giving a very insoluble, characteristic hydrochloride.

**Examination of the Hydrochloric Acid Solution.**—The mother liquor containing the other amino acids of nitro-fibroin (300 g.) was concentra-

<sup>1</sup> *Loc. cit.*

<sup>2</sup> Johnson and Kohmann, *Loc. cit.*

ted, after complete separation of 3-nitrotyrosine, to a thick syrup by heating in a vacuum at 100°. Absolute alcohol was then added in excess and the  $\alpha$ -amino acids esterified according to the directions given by Fischer.<sup>1</sup> Glycocoll was obtained in large amount in the form of its ester hydrochloride. The total yield of this salt was 141.5 g. and it melted at 144°. A mixture of this material with the pure hydrochloride of ethylaminoacetate melted at the same temperature.

Calc. for  $C_4H_{10}O_2NCl$ : N, 10.05. Found: N, 9.85, 9.97.

After complete separation of the hydrochloride of ethylaminoacetate the alcoholic filtrate was concentrated by heating under diminished pressure at 100° and the excess of alcohol removed. A black, syrupy residue was obtained which was diluted with one-half its volume of water and the hydrochloric acid neutralized at a low temperature by addition of 33% sodium hydroxide solution. The free amino acid esters were then extracted in the usual manner with ether after saturating the solution with potassium carbonate.<sup>2</sup> After drying carefully and removal of the ether, we obtained 50.7 g. of oil which was fractionally distilled under diminished pressure with the following result:

Fraction 1, 53–63° at 13 mm. = 21.50 g.

Fraction 2, 63–85° at 13 mm. = 24.00

Fraction 3, 85–95° at 15 mm. = 3.00

Total = 48.5

These fractions were saponified and examined for amino acids. Alanine was the only one identified. The usual tests for phenylalanine and leucine were applied to Fraction 3, but this gave, on saponification, nearly pure alanine. From the 3 fractions were obtained 30 grams of this  $\alpha$ -amino acid.

Calc. for  $C_3H_7O_2N$ : N, 15.75. Found: N, 15.90, 15.80.

The results obtained by hydrolysis are recorded in Table I.

TABLE I.

Percentages and Amounts of Amino Acids Produced by Hydrolysis of 300 g. of Nitro-fibroin.

Glycine ester hydrochloride.	Actual glycine.	% of glycine.	Nitrotyrosine hydrochloride. <sup>3</sup>	% of nitrotyrosine	Alanine.	% of alanine.	Oxalic acid.	Percentage of nitro-fibroin accounted for as glycine alanine and nitrotyrosine.
Grams.	Grams.	%.	Grams.	%.	Grams.	%.	Grams	%.
141.5	76.0	25.36	20.0	5.74	30.0	10.0	2.78	41.10

<sup>1</sup> *Z. physiol. Chem.*, 33, 177 (1901).

<sup>2</sup> Fischer, *L.c. cit.*

<sup>3</sup> It is important to note here that this represents pure nitrotyrosine hydrochloride. The actual quantity present was larger but it could not be completely separated on account of its solubility.

**Examination of the Nitric Acid Filtrate.**—After the separation of nitro-fibroin from the nitric acid, it was thoroughly washed with water and the washings added to the original strong nitric acid solution. This was not discarded by us, but submitted to a careful examination in order to determine its contents. It was of interest to determine whether it contained any characteristic products of oxidation, formed by the prolonged action of nitric acid, and also any nitrotyrosine and other amino acid constituents of the original fibroin. In order to avoid any further oxidation this solution was concentrated by pouring into shallow glazed pans and allowed to evaporate spontaneously at a temperature of 35°. A specially constructed oven was used for this purpose and the operation hastened by passing a swift current of air over the surface of the liquid. We obtained in this manner a yellow, viscous oil containing in suspension hard, dense crystals. In our analysis of this residue we applied the methods utilized by Mörner in his examination of the decomposition products obtained by intense treatment of protein material with strong nitric acid.<sup>1</sup> He demonstrated the formation of oxalic, picric, benzoic and *p*-nitrobenzoic acids and another acid of unknown constitution (*x*-säure) as products of the reaction. Following his directions in our work we were able to establish conclusively the presence of oxalic acid only. In fact, we found that practically the entire residue apart from the oxalic acid consisted of ammonium nitrate.

In a second experiment we modified our procedure and subjected the residue, after evaporation of nitric acid, to an esterification in order to determine whether any amino acids were dissolved in the liquor. This operation was not productive of any evidence that such combinations were present. In fact, after extraction with ether in the same manner and evaporating the solvent only a very small amount of resinous material was obtained. In other words, the nitric acid solution contained only end products of oxidation.

**Specific Rotation of Nitro-Fibroin.**—Fibroin is optically active and its rotatory power has been carefully measured by Vignon.<sup>2</sup> This investigator used hydrochloric acid as a solvent for his protein and determined the specific rotation of fibroins from nine different sources. His results were remarkably constant. This protein in every case was laevorotatory and the specific rotation ranged from  $-39.40^\circ$  to  $-48.20^\circ$ . We now find that our nitro-fibroin is likewise laevorotatory and that the specific rotation is about the same as that of pure fibroin. We obtained the values  $[\alpha]_{17}^D = -43.39^\circ$  and  $-44.10^\circ$ . Solution of the nitro-fibroin was effected by dissolving a weighed amount of the protein in 50

<sup>1</sup> *Z. physiol. Chem.*, **95**, 263 (1915).

<sup>2</sup> *Compt. rend.*, **113**, 802 (1891); **114**, 129 (1892); *Bull. soc. chim.*, [3] **7**, 139, 773, 799 (1892).

cc. of concentrated hydrochloric acid at  $0^{\circ}$  and then diluting to 100 cc. with distilled water. The solution was then filtered to clarify it. Several rotations were taken at  $17^{\circ}$  and remarkably constant results were obtained. In fact, the measurements ranged between the values recorded above.

While nitro-fibroin was found to be optically active, on the other hand, the alanine and 3-nitrotyrosine obtained by hydrolysis were both optically inactive. In this connection it is interesting to note that 3-nitrotyrosine, prepared from natural tyrosine (from silk) by action of nitric acid,<sup>1</sup> is likewise optically inactive.

### Summary.

Nitro-fibroin<sup>2</sup> has been hydrolyzed by digestion with hydrochloric acid and 41.10 per cent of its molecule accounted for in the form of glycocoll, alanine, and 3-nitrotyrosine. The protein is optically active, but on hydrolysis leads to the formation of optically inactive alanine and 3-nitrotyrosine. The relative proportion of tyrosine to alanine and glycocoll in silk fibroin is 1 : 2.1 : 3.6, while in our nitro-fibroin the ratio of nitrotyrosine to alanine and glycocoll is 1 : 1.7 : 4.4.

Tyrosine linked in fibroin is not attacked by nitric acid of specific gravity 1.12 at ordinary temperature with substitution of two nitro groups *ortho* to the phenolic hydroxyl group of this amino acid.

NEW HAVEN, CONN.

[CONTRIBUTION FROM THE BUREAU OF PLANT INDUSTRY.]

## VOLATILE OIL OF EUTHAMIA CAROLINIANA (L). GREENE.

By G. A. RUSSELL.

Received May 2, 1916.

*Euthamia Caroliniana* (L). Greene (Family Compositae), is found growing in moist, sandy old fields throughout the United States from Massachusetts to Florida and west as far as Texas. The plant is indigenous to these states and occurs in greatest abundance near the coast, especially in Florida. It is rarely ever found on new land or in woods, but is very frequently found in abundance in old, moist lake bottoms or abandoned fields. It flowers from September to November and each plant produces an abundance of small lemon-yellow blossoms.

**Distillation of the Volatile Oil.**—On September 8, 1914, Mr. S. C. Hood, scientific assistant in charge of the Florida station of the Office of Drug and Poisonous Plant Investigations of the Bureau of Plant Industry, distilled 83 kilograms of the fresh herb gathered just previous to the flowering stage. The material was gathered in old fields adjacent to the city of Orlando in Orange County, Fla. While yet in the fresh unwilted

<sup>1</sup> Johnson and Köhmann, *Loc. cit.*

<sup>2</sup> Johnson, Hill and O'Hara, *Ibid.*

state the plants were distilled and yielded 576 g. of oil. The yield calculated with reference to the fresh herb was 0.693%. The oil was pale yellow in color and possessed a pleasant aromatic odor.

On January 11, 1916, a chemical examination of the oil was undertaken. The color had not changed on storage. The odor was characteristic of the plant when crushed between the fingers, somewhat sweetly aromatic and not unpleasant. The taste was acrid, slightly bitter and left a strong terebinthinate after-taste manifested at the base of the tongue.

**Physical and Chemical Constants.**—The specific gravity of the oil at 23° was found to be 0.8587. The low figure pointed to a predominance of terpenes in the composition of the oil. The index of refraction was 1.4805 and the specific angle of rotation at 23° was  $-10^{\circ}48'$ .

No free acids were present in the sample of oil examined. The saponification value was 6.35, which is equivalent to 2.10% of esters calculated as acetate of  $C_{10}H_{18}O(CH_3COOC_{10}H_{17})$ . The acetylation value was 25.3, which on calculation reveals 7.01% of alcohols in the original oil. The ester number of 6.35 is equivalent to only 1.66% of alcohols. There are, therefore, 5.35% of free alcohols (as  $C_{10}H_{18}O$ ) in the original oil.

**Solubility of the Oil.**—The oil was readily soluble in 6 volumes of 90% alcohol and clear in excess. It was also soluble, with slight cloudiness, in 9 volumes of 70% alcohol, and did not become clear on adding an excess of 50 volumes. The solubility results all point to a considerable quantity of terpenes present in the oil.

**Tests for Phenols and Aldehydes.**—Five cubic centimeters of oil were shaken with a 5% solution of sodium hydroxide and the mixture allowed to stand for twenty-four hours. No diminution was noted in the volume of oil. The alkaline solution was then removed, acidified with sulfuric acid and distilled with steam. The distillate tested with ferric chloride gave negative results. There were no phenols present in the sample of oil examined.

A quantitative test with Schiff's reagent revealed the presence of aldehydes. The characteristic purple color was produced after the mixture of oil and reagent had stood for about thirty minutes. A small amount of aldehydes was present in the oil.

**Combined Acids in the Oil.**—A portion of the oil was saponified with alcoholic potassium hydroxide; water was added and the whole heated on a water bath until the alcohol was expelled. The oil which separated out was removed and the aqueous alkaline solution shaken out with ether to remove any adhering oil. The alkaline solution was then reduced to a small volume on a water bath, treated with an excess of sulfuric acid and distilled with steam. The distillate was found acid to litmus and possessed a sharp though not a marked disagreeable odor. The distillate

was neutralized with 0.02 *N* potassium hydroxide and precipitated with 0.1 *N* silver nitrate. Reduction of the silver salt took place almost immediately. From the odor of the distillate, the nonseparation of oily globules on the same, and the quick reduction of the silver salt, the conclusion is drawn that the combined acid or acids present are low in carbon content and consist probably of esters of acids lower in carbon content than propionic acid.

**Fractionation of the Oil.**—A portion of the oil was first saponified and then fractionated under atmospheric pressure. Fractionation was carried on in a 200 cc. round bottom flask fitted with a Hempel distilling column having a neck 10 centimeters in length from constriction to delivery tube. The neck was filled three-fourths full with glass beads. Heat was applied by means of an air bath. An Anschütz thermometer was used and no corrections of temperatures were made.

TABLE I.—FRACTIONATION OF THE SAPONIFIED OIL.

Fraction.	Temperature.	Per cent. distilled.	Color.	Odor.	Density at 23°.	$[\alpha]_D$ at 23°.	$N_D$ at 23°.
1	170°	1.52	Water white	Slight odor of pinene	0.7992	...	1.4663
2	170–175°	51.44	Water white	Sweetly aromatic	0.8414	–3° 3'	1.4756
3	175–177°	18.04	Water white	Sweetly aromatic	0.8431	–4° 6'	1.4770
4	177–179°	9.42	Water white	Sweetly aromatic	0.8461	+13° 0'	1.4770
5	179–185°	0.50	Light yellow	Somewhat decomposed	..	...	..
6	185°+	19.58	Dark brown	Decomposed	..	...	..

Since the results obtained by fractionating the saponified oil pointed to the presence of an abundance of one constituent in this oil, a small portion of the original oil was fractionated under atmospheric pressure. The same distilling apparatus and the same source of heat was employed as in the fractionation of the saponified oil.

TABLE II.—FRACTIONATION OF THE ORIGINAL OIL.

Fraction.	Temperature.	Per cent. distilled.	Color.	Odor.	Density at 23° C.	$[\alpha]_D$ at 23°.	$N_D$ at 23°.
1	176°	50	Water white	Sweetly aromatic	0.8435	–2° 6'	1.4742
2	176–180°	25	Water white	Sweetly aromatic	0.8660	+9° 36'	1.4814
3	180°+	25	Yellowish brown	Slightly decomposed	..	...	..

A third portion of the original oil was then fractionated under 45 mm. of pressure and eight fractions secured. Heat was applied by means of an air bath and the same distilling apparatus used as in the previous fractionations.

**Examination of the Fractions.**—Fraction 1, which possessed a slight odor of pinene was tested by means of the nitrosochloride reaction.<sup>1</sup> A deep blue coloration was obtained on adding 22% of the prescribed amount of hydrochloric acid. On further addition of this reagent the color disappeared. The pinene in the oil is present only in a minute amount.

<sup>1</sup> O. Wallach, *Annalen der Chemie*, Vol. 245, p. 251.

TABLE III.—FRACTIONATION AT THE ORIGINAL OIL UNDER 45 Mm. PRESSURE.

Fraction.	Tem- perature.	Per cent. distilled.	Color.	Odor.	Density at 23°.	$[\alpha]_D$ at 23°.	$N_D$ at 23°.
				Slight odor of			
1	79-91°	5	Water white	pinene	0.8438	.....	..
	91-92°	12					
	92-93°	13					
	93-94°	17.1					
	94-95°	5					
2	91-95°	47.1	Water white	Aromatic	0.8439	— 3° 36'	1.4765
	95-96°	8					
	96-97°	6					
	97-98°	2.9					
	98-100°	1.0					
3	95-100°	17.9	Water white	Aromatic	0.8444	— 3° 36'	1.4795
4	100-105°	5	Water white	Aromatic	0.8470	+ 5° 18'	1.4844
5	105-115°	5.4	Light yellow	Aromatic	0.8669	+19° 48'	1.4878
6	115-150°	4.6	Light yellow	Sweet aromatic	0.9056	—34° 18'	1.4937
7	150-180° <sup>1</sup>	5	Yellow	Slightly decom- posed	0.9286	—63° 18'	1.5042
8	Residue	10	Dark reddish brown	Slightly decom- posed	..	.....	..

A purple color developed on allowing a portion of the fraction to stand in contact with Schiff's reagent for thirty minutes, indicating a trace of aldehydes.

Fractions 2, 3 and 4, which contain the major portion of the fractional oil, were examined for dipentene. Wallach<sup>2</sup> gives the following constants for dipentene: B. p., 177-178°; Sp. gr., 0.845 at 20°.

The boiling point of the major portion of the oil was found to be 170° to 179°, 80.42% passing over at these temperatures. The specific gravity of the fractions obtained at atmospheric pressure was from 0.8414 to 0.8461 at 23°. A more careful fractionation at 45 mm. pressure gave fractions whose specific gravity at 23° was 0.8439 to 0.8444, which corresponds very closely with those stated in the literature.

On shaking a portion of the fractions with an equal volume of concentrated sulfuric acid, a strong odor of hydrogen sulfide was developed, indicating the presence of dipentene.<sup>3</sup>

On treating these fractions with alcoholic sulfuric acid at a temperature of 50° a compound was obtained that had no optical activity.

A weighed amount of each of the fractions was treated with bromine. After standing for several days crystals separated out. These crystals of dipentene tetrabromide recrystallized from acetic ether melted at 123-124°. The fraction consist mainly of dipentene.

<sup>1</sup> At 180° decomposition becomes marked as indicated by a sudden fall in the temperature.

<sup>2</sup> *Ann.*, 245, 197.

<sup>3</sup> Heusler and Pond, "Chemistry of the Terpenes," 89 (edition).

On shaking Fraction 5 with an equal volume of concentrated sulfuric acid a slight odor of hydrogen sulfide was noted. On treating with bromine a slight amount was absorbed, but no crystals separated on standing. Testing for limonene by means of the nitrosochloride gave a blue coloration at first, but this color rapidly disappeared. Evidently there is little, if any, limonene in the oil.

Fractions 6 and 7, which consist of 9.6% of the original oil, are levorotatory and of relatively high specific gravity. Their composition was not established.

### Summary.

The sample of volatile oil of *Euthamia caroliniana* (L). Greene examined, consists mainly of dipentene with a trace of pinene and possibly a small amount of limonene. No free acids were present, although the oil had been distilled and stored for about 15 months. A small percentage of combined acids, probably formic and acetic were present. Esters were present to the extent of 2.10% calculated as  $\text{CH}_3\text{COOC}_{10}\text{H}_{17}$ . The presence of aldehydes was established by means of Schiff's reagent. The total amount of alcohols present was 7.01%, of which 5.35% are free, and 1.66% combined. In addition to the compounds identified, a compound or compounds having levorotatory properties and a comparatively high density, are present to the extent of approximately 10%. That portion of the sample of oil that boiled above  $180^\circ$  at 45 mm. pressure with decomposition constitutes approximately 10% of the volume of the original oil.

BUREAU OF PLANT INDUSTRY,  
WASHINGTON, D. C.

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## THE CHEMICAL COMPOSITION OF OSCILLARIA PROLIFICA.

By B. B. TURNER.<sup>1</sup>

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This plant, one of the *Cyanophyceae*, was first brought to the attention of the previous authors in connection with the systematic examination of the public water supplies of Massachusetts under the direction of the State Board of Health. This study was undertaken and carried on for a number of years prior to Mrs. Richards' death, because the plant is a type of blue-grass alga that has caused much trouble at water works and to consumers. It was felt that by a study of the plant some plan could be devised for successfully dealing with the class.

The life history and chemical composition of the alga have already been the subject of three papers.<sup>2</sup> It is there described how the alga

<sup>1</sup> This work was made possible through a fund established as a memorial to the late Ellen H. Richards.

<sup>2</sup> Isabel F. Hyams and Ellen H. Richards, *Technology Quarterly*, 14, 302 (1901); 15, 308 (1902); 17, 270 (1904).



grew in great quantities in the water of Jamaica Pond near Boston and contaminated the water supply, till it was destroyed by treatment with copper sulfate. The present paper is a continuation of the work on the chemical constitution of the organism begun by the former authors, and many of the lines followed were suggested by them.

The material available at this time consisted of some kilograms of the dead alga, partly dried and partly preserved in various liquids, particularly in alcohol and in glycerol. Some of the samples labelled "fermented" had evidently been put up after undergoing partial decay on exposure to air. As the samples were all several years old, it was not possible to be sure than some of the smell and fermentative processes which had gone on in those samples free from preservatives, were not partly due to moulds and other organisms which had grown somewhat upon the dead material. It is not believed, however, that the changes from this source, in the tightly-closed bottles, had been great.

**Composition in General.**—Using the ordinary methods of analysis of foodstuffs, it was found that the air-dried material contained 9.7% of moisture and 6.4% of ash, in close agreement with earlier work. A small part of the latter is due to fine sand unavoidably collected with the alga.

The proportion of nitrogen was found by the Kjeldahl method to be 7.4%, equivalent to 46.25% of protein by the usual factor of 6.25. The dried alga was next extracted with ether in a Soxhlet's apparatus, whereby 2.2% was removed. The extract contained some chlorophyll and a very small amount of fat.

The remaining 35.5% consisted principally of carbohydrates, as will be shown later, along with which would be included the more or less insoluble and indigestible substances usually classed as "fiber."

**Extractions with Solvents.**—Since ether extracts comparatively little, in order to study the nature of the material extracted it was necessary to submit a large quantity of the alga to the action of the solvent.

For this purpose an apparatus was devised by which any ordinary flask could be used and an intermittent flow obtained as in the Soxhlet extractor. As it is thought that this may prove useful to other investigators who have to work with large quantities of material, it is here described in detail.

**New Form of Extraction Apparatus.**—In order to obtain the same action as in a Soxhlet's extractor without using a flask having an outlet or side tube below the level of the neck, it is only necessary to use a siphon with equal limbs and upturned ends, so as never to run dry, at the height of the upper level to which the flask is to be allowed to fill, enclosed in another siphon, the inner limb of which reaches to the bottom of the flask, the outer limb being still lower. The air in the outer siphon, above the level of the ends of the inner siphon, is always at the same pressure in

both limbs, since they communicate freely, and this pressure varies with the action of the outer siphon, becoming lower by the expansion of the enclosed air as the liquid in the flask runs down when the siphon is in action, just as the pressure of a bubble of air trapped in the bend of an ordinary

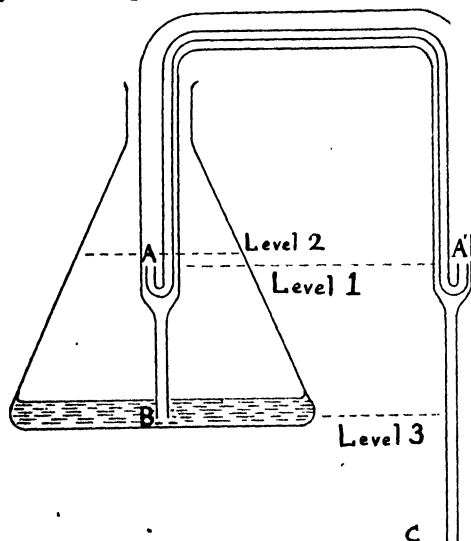


Fig. 1.

siphon would do. The principle and manner of action of the siphon is shown diagrammatically in the accompanying sketch. The inner siphon, once filled, will remain full of liquid since the open ends A and A' are on the same level 1 and higher than the bends down which the liquid would have to flow to empty the siphon. As the liquid accumulates in the flask, the outer siphon being empty and the outer limb open to the air at C, it will rise in the limb AB level with the surface of the liquid in the flask, till it reaches level 2, a little above that of the end A when the inner siphon will come into action and carry the liquid over to A', and so fill the outer limb A'C. This will reduce the pressure of air in the upper part of the outer siphon, carrying over the extra volume due to expansion and the liquid will now be drawn out of the flask as by an ordinary siphon, flowing up to A even when the level in the flask has sunk below level 1, by atmospheric pressure, passing over to A' by the inner siphon and then descending to C. This will, obviously, continue till the flask is emptied down to level 3 when air will enter at B, and passing by the upturned end of the inner siphon A, restore the atmospheric pressure in the outer siphon causing the outer limb A'C to empty itself, when the action of the siphon will be broken, allowing the liquid again to accumulate gradually in the flask till it once more reaches level 1. This double siphon will therefore act just like the intermittent siphon in a Soxhlet apparatus, though there is no communication through the walls of the flask below the level of the neck.

In practice, the siphon is made as in the accompanying sketch, the upturned ends of the inner siphon being replaced by cups at A and A', which rest by means of small knobs of glass fused to them, on the constricted part of the outer tubes without closing the same. At D and D', the inner tubes are fused into the wider tubes, which are connected at E and F by a cross tube sealed into both. It was also found advan-

tageous to have at G, where the narrower is joined to the wider part of the inner limb, a small jet, projecting inwards, and turned a little to one side so that when the siphon empties, the inrush of air from B may be divided into small bubbles and directed past the cup at A without risk of forcing its way into the inner siphon, as may happen if the free passage of the bubbles is obstructed. The outer tubes must not be too wide, nor the inner ones too narrow, as a large volume of air in the outer siphon delays, by its expansion, the filling of the outer limb A'C, while, if the inner tubes are not wide enough to allow a fairly rapid flow of liquid from one cup to another, the outer limb may not fill at all, but the liquid may continue gradually trickling over, in which case the level of liquid in the flask cannot be drawn down below that of the cups. When properly proportioned the apparatus works well for long periods. The stopcock K is introduced for convenience in filling. If the siphon is fitted up so that V is beneath the level of liquid in the outer flask or reservoir, then as soon as the inner flask fills up to the level of B, a slight suction through K will fill the inner siphon, when K is closed and the subsequent action is automatic.

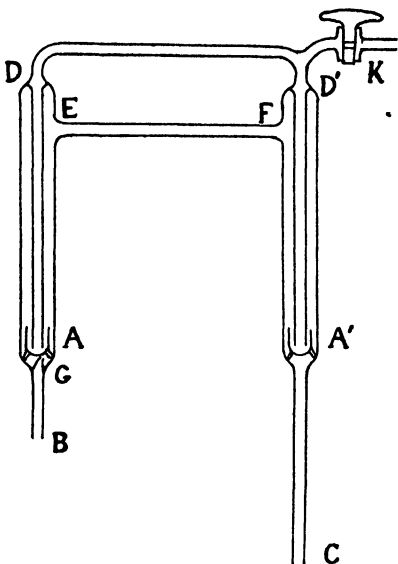


Fig. 2.

A form of the same apparatus which is easier to construct, may be made by using corks at D and D' in place of the sealed joints, and making the outer siphon in two parts connected by a rubber joint on the tube EF.

**Extraction with Alcohol.**—Extraction of the air-dried material with petroleum spirit (boiling at 40–60°) gave only about 0.1% of extracted matter, and ethyl ether extracted, as stated above, only about 2.2%.

Extraction with alcohol yields larger quantities of material.

The samples of *oscillaria* which had been standing several years in "strong" alcohol still contained a large amount of substance which could be extracted by that solvent. A portion of this partially extracted alga, after draining off the liquid, which weighed 25 g. when air-dry, was triturated in a mortar with successive quantities of about 30 cc. of absolute alcohol as long as the green color remained. After about twenty such operations, the combined extracts were mixed and an aliquot part evaporated to dryness. In this manner 1.66 g. was found to have been ex-

tracted. Allowing for moisture in the air-dried sample, and loss in the process of decanting and filtering, about 7 to 8% of the substance is seen to be soluble in cold absolute alcohol.

If the alga is treated with hot alcohol containing some water, the amount extracted is not so great. In four treatments of 100 g. of dried alga with 150 to 200 cc. of 80% alcohol, the total filtrate contained only 2.9%. If this treatment is now followed by absolute alcohol, very little more is extracted, about 0.1%. The larger amount extracted in the cold appears to be due to some coagulation, or other change, caused by the heat, which renders some constituents insoluble.

Cold water in repeated treatments extracted about 12.5%. If the aqueous extraction was preceded by alcohol, the amount withdrawn by the water was a little less. In four extractions of a lot of 100 g., following on the treatment with 80% alcohol and absolute alcohol described above, a total of 12.18% was obtained.

Boiling water acting directly on the original *oscillaria* extracted very little, but a characteristic swelling of the mass occurs to a voluminous jelly, about ten times the volume originally occupied by the solid in the loose, moist state. At the same time, the filtrate which first comes through soon gelatinizes. The carbohydrate of the alga seems to consist largely of a pectin-like substance.

The cold water extract is of a pale straw color, and rotates the plane of polarization of light to the right. It gives no precipitate on boiling the slightly acidified solution, but gives a slight yellow coloration with nitric acid. Saturation with ammonium sulfate causes a precipitate to form, as does phosphotungstic acid. Proteoses appear, therefore, to be present. The chief constituent present is apparently a carbohydrate which is dextrorotary but has little action on Fehling's solution until hydrolyzed by boiling with acids, when it causes copious reduction. The same action reduces the positive rotation, in case of prolonged treatment with acid, to zero or somewhat below.

The residue from aqueous extraction was then treated with acids. Dilute hydrochloric or sulfuric acid (1 to 2%) acts on the carbohydrate present very slowly. Accordingly, recourse was had to 5% sulfuric acid and digestion on the water bath (at about 96°) for from 6 to 10 hours at a time. This process not only hydrolyzed and dissolved carbohydrates but also decomposed proteins and the resulting liquid therefore gave a copious precipitate with phosphotungstic acid.

**Carbohydrates.**—The following experiments indicate the nature of the carbohydrates present. One hundred grams of air-dried *oscillaria* were extracted with 600 cc. of distilled water, protecting the extract from bacteria by a little toluene. The filtered extract, after precipitation with basic lead acetate and removal of excess of lead by  $\text{Na}_2\text{CO}_3$  ( $\text{H}_2\text{S}$  leads to solu-

tions which are almost impossible to free from colloiddally suspended lead sulfide) and neutralizing contained by Fehling test, reducing sugar equivalent to 0.171 g. dextrose. The rotation was  $+0.40^\circ$  for 1 decimeter.

Other similar aqueous extractions showed an average rotation of about  $+0.4^\circ$  and a cupric reducing power of about 0.001–0.002 g. per cc.

The residue from the aqueous extraction was then treated with successive quantities of about 800 cc. 5%  $\text{H}_2\text{SO}_4$  on the water bath for periods of about 10 hours. The first acid extract neutralized with  $\text{CaCO}_3$  and filtered measured about 500 cc. and showed the high rotation  $+2.35^\circ$ . After removal of sulfates by  $\text{BaCl}_2$  addition of basic lead acetate gave a copious, flocculent white precipitate. After removing excess of lead with  $\text{Na}_2\text{CO}_3$  and neutralizing, the solution, made up to 500 cc. in a measuring flask, showed a rotation of only  $+0.965^\circ$ . This solution contained 0.0476 g. per 1 cc. total solids, and had a reducing power equivalent to 0.005 g. dextrose per 1 cc., or a total of 2.5 g. By further heating for 6 hours with 5%  $\text{H}_2\text{SO}_4$ , its rotation was reduced to  $+0.475^\circ$  (for the same volume) and its reducing power rose to 0.0075 g. per 1 cc. of the original volume.

By heating with phenylhydrazine hydrochloride and sodium acetate on the water bath for several hours, a small quantity of a crystalline precipitate was obtained from the above solution which showed a rotation of  $+2.35^\circ$ . This, when crystallized from 50% alcohol with a little pyridine, melted, when rapidly heated, at  $217\text{--}218^\circ$  (corr.). Recrystallized from the same solvent, it formed beautiful clusters of very minute yellow needles, and melted sharply at  $217^\circ$ . The quantity obtained was too small for complete analysis, or further investigation, but a microkjeldahl analysis with 0.0056 g. of the once crystallized substance gave 0.00062 g. nitrogen, equivalent to 11.7%. This agrees with the formula of a hydrazone of a hexose ( $\text{C}_6\text{H}_{12}\text{O}_5\cdot\text{N}_2\text{HC}_6\text{H}_5$  N = 10.37%), or the osazone of a disaccharide ( $\text{C}_{12}\text{H}_{20}\text{O}_9\cdot(\text{N}_2\text{HC}_6\text{H}_5)_2$  N = 10.77%), rather than an osazone of a hexose ( $\text{C}_6\text{H}_{10}\text{O}_4\cdot(\text{N}_2\text{HC}_6\text{H}_5)_2$  N = 15.64%), but no known compound could be found with this melting point, containing less than two phenyl hydrazine groups to one (monosaccharide) sugar radical. Inactive  $\alpha$ -acrosazone, with the last formula, melts at this temperature, while a galaheptose-bisphenylhydrazone (N = 14.43%) melts at about  $218^\circ$ . The high positive rotation of the above solution seems therefore to be due to a disaccharide of unknown composition which, on further hydrolysis, is slowly split up into monosaccharides with a much smaller rotation. The slowness of hydrolysis negatives the existence of any disaccharide such as maltose or galactose, and as solutions with a negative rotation of any considerable amount were not obtained (see below); this still further excludes the presence of saccharose.

Qualitative tests for pentoses with phloroglucin and orcin gave nega-

tive results, as also did the resorcin test for levulose (and indirectly, for saccharose).

**Volatile Matter.**—As the unpleasant odor acquired by the water in which the oscillaria was found was one of the reasons on account of which its investigation was first begun, a method was sought by which the volatile matters might be isolated. The smell of the unfermented oscillaria, in the dry state, is pungent but not unpleasant, and seems to be due to the aromatic substance soluble in petroleum spirit.

The fermented oscillaria, both that which had been put up in glycerol and that bottle without preservative, had a smell of decaying proteins and bad cheese. A quantity of the former was placed in a large flask, and the volatile substance present driven over with steam. The first portions of the distillate had the odor of feces, but later on, the smell changed to that of Limburger and Roquefort cheese, while it finally became more spicy, something like dried herring. The presence of indole and skatole were suspected in the first runnings, so these were shaken with ether. On filtering and evaporating the ether, only a small residue remained, from which the fecal odor had nearly disappeared, and no positive test for skatole could be obtained. The residue was chiefly of a fatty nature and showed microscopic needles. Indole and skatole, if present, as was strongly indicated by the smell, were plainly present in only very small quantities, and on account of their evanescent nature, the attempt to isolate them was not pursued further.

The bulk of the volatile substance present, which formed the chief cause of the offensive odor, consisted of fatty acids. By systematic extraction with ether of large quantities of steam distillate, two or three grams of these were obtained. An analysis of the barium salt showed that the acid was chiefly butyric.

**Saponin.**—The presence of a saponin-like substance in oscillaria prolifica is mentioned in an earlier paper,<sup>1</sup> "which is set free" (from the alga in its natural habitat) "to such an extent that the water froths whenever stirred by the wind, as if it contained a liberal supply of soap bark." A similar tendency to froth is easily noticed in the aqueous extract of the dried or preserved alga. But the suggestion that this tendency is due to a true saponin has not been confirmed by subsequent work. Various substances of the nature of dextrans, etc., might produce a similar result.

Since methyl alcohol constitutes the best solvent for saponin, 200 cc. were allowed to stand eleven days on 75 g. of dried, powdered oscillaria which had been previously extracted with ether. After filtering the deep green extract, ether was added to precipitate the saponin. A small quantity of a white gelatinous precipitate came down on adding about one volume of ether and this was increased a little by adding another volume

<sup>1</sup> *Tech. Quart.*, 15, 309-310 (1902).

of ether. A similar precipitate in about the same quantity was obtained by the action of methyl alcohol on the original dried oscillaria. This was tested for saponin in the following ways: (1) Basic lead acetate added to a solution of the above white substance gave no precipitate; (2) concentrated barium hydroxide solution gave a slight turbidity to a fairly strong solution; (3) ferric chloride and a ferricyanide was slowly reduced in the cold, somewhat faster on heating. This would agree with the presence of some saponin, as would the following two tests: (4) Mercuric chloride on heating and cooling gave with the substance in question a white turbidity; it was, however, *not* blackened by ammonia; (5) similarly, Nessler's solution was turned yellow, and, finally, gray, by this substance on heating; (6) tannic acid gave a considerable white precipitate; (7) no blue or green color, or fluorescence, however, was obtained on adding concentrated  $\text{H}_2\text{SO}_4$  with a little alcohol, likewise (8) no green color appeared on exposure to air of a solution of the substance in concentrated  $\text{H}_2\text{SO}_4$ ; (9) lastly, the hemolysis test proved negative in three to four hours; a slight hemolysis after sixteen hours was no more than would be observed with water alone. On the whole, the indications for the presence of an appreciable quantity of saponin in the oscillaria seem very doubtful. The substance isolated by methyl alcohol, which may also be the cause of the frothing, appears to be either a complex polysaccharide or more probably a glucoside. It does not reduce Fehling's solution directly, but does so strongly after it has been hydrolyzed by boiling for one-half to one hour with about 5%  $\text{HCl}$ .

A similar substance was found as a considerable constituent in all the alcoholic solutions in which the oscillaria had been preserved. These, though originally "strong" alcohol, had been diluted by the water in the fresh alga, so that they were not much more than 80%, in which strength saponin and similar substances are readily soluble.

**Crystals.**—A large part of the research was devoted to the search for definite substances which might be separated from the alga by crystallization. The various procedures need not be repeated in detail. With the exception of a few crystals of ammonium magnesium phosphate, only one crystalline substance was found and that in very minute proportion. This was obtained from the aqueous extract of the fermented oscillaria after it had been distilled with steam. The extract was treated with excess of basic lead acetate, a large quantity of gummy, brown precipitate was filtered off, the excess of lead removed with  $\text{H}_2\text{S}$  and the latter boiled off, and the filtrate then treated with about 2.5 volumes absolute alcohol, which brought down another amorphous precipitate. The filtrate from this was treated with ether till a slight turbidity was formed and then allowed to stand. Among the gummy drops which settled out in one or two days were found minute white spherules and star-shaped aggregates of

almost microscopic needles. By resolution of these in a very little water and reprecipitation with alcohol, and ether, they were obtained nearly free from gum, and the final separation was effected by rapid washing with water and decantation. By the microkjeldahl process described below, they were found to be free from nitrogen. When ignited in a little platinum boat, the ash was found to be 17.4%, consisting almost entirely of magnesia. The equivalent weight of the acid, assumed to be monobasic, is about 118, which agrees with that of caproic acid,  $C_6H_{14}O_2$ .

**Coloring Matter.**—Extraction with alcohol or ether of the air-dried alga, as well as that which had been preserved in alcohol, gave a brownish green solution characterized by a spectrum with five absorption bands. That this is caused by a mixture of two or more substances is shown by the separation of the bands, as indicated below. The original spectrum is as follows, the first four bands being given in the order of their intensity:

I. A very dark band with sharp edges in the red, extending in solutions of a medium depth of color, from about wave length 680 to 645  $\mu$ .

II. A broad, fairly dark band in the bluish green, shading off gradually from about 513 to 493.

III. A fainter band in the orange, shading off, 625 to 600.

IV. A faint band in the green, 540 to 530.

V. A strong end absorption beginning fairly sharply at about 440.

Of these, I, III, IV and V agree with Bands I, II, IV and VI, as given for crystallized chlorophyll by Willstätter.<sup>1</sup> Like other samples of "chlorophyll," this substance can be separated into a green coloring matter (the purified chlorophyll) and one or more yellow substances, such as have been described as xanthophylls.

Traces of yellow and red colors were observed at various times when the oscillaria was treated with solvents, but in too small amounts to allow identification.

The most interesting color obtained, however, was seen to a slight extent (perhaps as a colloidal suspension) in the aqueous extract of the air-dried material, which in bulk showed the violet color described in a former paper,<sup>2</sup> reproduced as No. 3 on Plate 1, but was present in notable quantity only in one bottle in which the oscillaria had been preserved under glycerol. Attempts to reproduce this by making glycerol extracts of the dried material all failed. Probably it is necessary to extract the fresh oscillaria with glycerol at a certain state of its growth, or exposure to air, or it may be that some ferment is concerned in the liberation of the color, which has lost its activity in the years since the alga was collected. Adding a little of the colored solution to a fresh glycerol extraction did not affect the result.

<sup>1</sup> *Handbuch d. Bioch. Arbeitsmethoden* II, p. 683.

<sup>2</sup> *Tech. Quart.*, 17, 3, 271 (1904).



The glycerol solution already mentioned was a deep bluish green by transmitted light, but was characterized by an intense red fluorescence, so that when looked at in bulk, or even in thin layers when illuminated from the side or behind the observer, it looked like blood. This fluorescence was examined with monochromatic illumination and showed a narrow band in the red at  $670\mu\mu$  which appeared unchanged in position when the wave length of the illumination varied, provided, as is required by theory, that the latter was shorter than that of the band; for longer wave lengths of illuminating light, the fluorescence disappeared.

The absorption spectrum of the blue-green solution was as follows:

I. Very dark band in red with a sharp edge on the red side at about 658 (shading at most to 660 or 662), and shading very gradually on the yellow side from about 643 almost to the D lines (*i. e.*, to about 600).

II. A very faint band in the yellowish green at about 577 to 565.

III. End absorption commencing about 450 and strong from 440 onwards.

Of these the third seems to be due to admixture with a green "chlorophyll," like that already described, as it disappears on purification, as appears in the following; the second agrees in position with Band III of Tswett's<sup>1</sup> Chlorophyllin  $\alpha$ .

Both ether and alcohol precipitate the color, but it is changed in the process. The precipitate has a purple hue but is much less intensely colored than the original solution. Acids and alkalies also destroy the color. Heating to about  $70^{\circ}$  causes a highly colored dull blue flocculent precipitate to collect, as also does the addition of lead acetate, but in neither case can the coloring matter be redissolved unchanged.

When the glycerol solution is mixed with about two-thirds of its volume of a saturated solution of ammonium sulfate, the coloring matter is precipitated, which precipitate may be readily redissolved, after filtration, on adding a little distilled water. It then shows a pure blue color and the same intense red fluorescence. Repetition of the process requires a greater concentration of ammonium sulfate, as the glycerol has been removed, but the substance comes down readily on saturating its aqueous solution with the salt. In this way, it may be obtained in solution free from glycerol.

The color may be purified by precipitation with ammonium sulfate, and the spectrum of this purified solution, which is a pure and very intense blue in color, strongly resembling in appearance the color of cuprammonium hydroxide, shows Band I as described, very strongly without the end absorption III.

This blue coloring matter with the strong red fluorescence, for which the name "algocyan" is proposed, is of a very labile character. It keeps fairly well in aqueous solution (in presence of some ammonium sulfate)

<sup>1</sup> *Handbuch Bioch. Arb. Meth.*, II, p. 691.

if covered with toluene, but slowly fades on exposure to light for some days. Strong mineral acids or alkalies in solution of 1%, or more, decolorize it rapidly, producing a slight white precipitate. The same effect is produced, but more slowly by alcohol. If this be added gradually, there is no perceptible change at 10 or 15%, but when 50% is reached the solution, though still blue, has lost its fluorescence and appears very faintly turbid. The disappearance of the fluorescence seems to coincide with the change of state of the substance from solution to colloidal suspension. Addition of water at this stage does *not* redissolve the substance, and the fluorescence does not reappear. The algocyan is "denatured." Further addition of alcohol causes coagulation of the precipitate; if this be filtered off at once, it may be redissolved in *very* dilute ammonia (about 1 in 1000) but is bleached almost instantly. The neutral solution of unaltered algocyan in water is similarly bleached by ammonia, though a few drops per 1 cc. of 1 in 100  $\text{NH}_4\text{OH}$  may be added without affecting the color or fluorescence. The coloring matter is not carried down by ammonium magnesium phosphate in the solution. The fluorescence is destroyed by dilute acetic acid, indicating that the solution has been changed to a colloidal suspension, as when alcohol is added, but there is a difference in this case, as the fluorescence reappears on adding dilute ammonia till the substance redissolves.

Dilute ferric chloride added cautiously (1 or 2 drops of 1 in 300 solution to each 1 cc. of very deep blue solution of algocyan) precipitates a substance apparently as blue as the original, which redissolves in very dilute ammonia (1 in 1000) to a violet solution of a paler color, from which saturation with ammonium sulfate precipitates a dull blue substance with apparent loss of color.

#### Microkjeldahl Method.

The well known Kjeldahl method for the estimation of nitrogen, as ordinarily carried out, requires the sacrifice of one or two decigrams, or more, of material for each determination. Where only very small quantities of substance are available, satisfactory results can still be obtained by a modification of the details of manipulation. After some experimentation, a method was found which would yield useful information as to the nature of a substance by the analysis of from 5 to 10 mg., and with care should give results accurate to about 1%, or even less, with such minute quantities. While the modifications introduced are only of the nature of details, the great usefulness of a method of obtaining such information, when obliged to work with almost "microchemical" quantities, seems to make it advisable to publish those details here.

For such minute quantities of material, the amount of sulfuric acid taken must be correspondingly reduced, not only to avoid an appreciable error in the correction for the nitrogen in the "blank," but chiefly to re-

duce the volume of the total liquids in the distillation. Half a cubic centimeter of concentrated sulfuric acid was taken each time, measured in a capillary pipet graduated to hundredths, about 0.5 g.  $K_2SO_4$ , and, when necessary to accelerate digestion, one milligram of mercuric oxide. The digestion was performed in a test tube of about one centimeter diameter in the end of which a bulb about 1 inch in diameter had been blown, which gave a space of about 10 cc. for the bursting of the bubbles should the liquid begin to "bump." The tube was used in an inclined position so that the drops should be thrown against the sides, but in spite of this precaution, bumping was the commonest source of trouble in the method and great difficulty was experienced in avoiding errors from this cause. While a slight bumping might occur without introducing serious error, it only needed the loss of a very small drop, where such minute quantities were used, to make the results entirely misleading. However, by the use of a specially small "microburner" in heating, the liquid could usually be made to boil steadily with minute bubbles, or to digest at a temperature a little below its boiling point. For this purpose, a pinhole flame may be used, by burning ordinary gas from a glass capillary about one millimeter in diameter, but besides covering the bulb with soot, the yellow flame was found inferior in another way to that about to be described. To obtain a concentrated heat at a very small point, which is the least likely to cause bumping, and will not boil the acid too rapidly, a blue flame on the principle of the Bunsen burner, not exceeding 6 to 8 millimeters high and 3 or 4 in diameter, was obtained by using a burner, easily made from glass tubing, of the shape and size shown in the sketch. The glass jet A is sealed at B into another piece of tubing BC, in which a slight expansion has been blown just below the point to which the end of the jet A will reach, and in the opposite sides of this expansion, two thin-walled bulbs at D,D. These are then crushed by a smart blow and the edges of the holes rounded in the blow pipe. The opening at C is drawn out to about three millimeters diameter. The size of the air holes at D,D is not very material. They cannot, of course, be regulated, according to the size of the flame, as in an ordinary burner, but for small flames, the inflow of air is nearly self-regulating as the flow of gas alters and there is no danger of the flow "striking back." It was found, how-

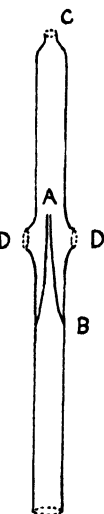


Fig. 3.

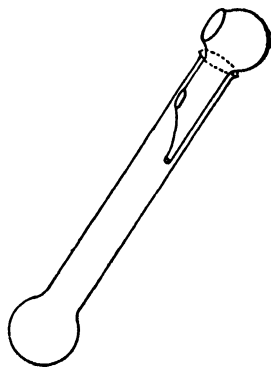


Fig. 4.

ever, that the flames were often insufficiently oxygenated, however wide the air holes were made, owing to the jet A being too wide, so that the gas did not issue at a high enough velocity to draw in the air required. Care must be taken, therefore, to make this hole small enough, while not so small that the maximum flame, when the gas stopcock is turned full on, is less than that mentioned above. The easiest way to ensure this is to test the jet with full gas pressure before sealing it in: if the yellow flame so obtained is about a centimeter long, the hole is of the right size; if larger, it may be readily contracted by cautious heating of the edges in the blow pipe. A properly adjusted burner gives, with the gas full on, a bright blue flame like that of an ordinary burner which has a slight over-supply of air, about 10 to 12 mm. high; and this can be reduced to half the height without danger of extinction or turning yellowish. In use, the flame is placed close up to the bulb to be heated so that its point just touches the glass, adjusting it carefully beneath the part covered by the acid. If the glass towards the edge of the liquid be directly heated, there is a steadier evolution of bubbles and less tendency to bump, but loss of experiments by cracking of the bulbs is very frequent.

To obviate further the danger of loss by spurting out of minute drops, it was found advisable to place a funnel in the mouth of the tube. An ordinary funnel soon becomes sealed by drops of condensed liquid, which are then spurted out by each sudden evolution of vapor, so a form was designed in which a free passage to the outer air would always remain open, while no drops could possibly be spurted straight through. This consisted in a piece of glass tube just narrow enough to slip easily into the mouth of the test tube with a spherical bulb about 5 mm. wider in diameter blown on the upper end, in which a large round hole, like the opening of a thistle-funnel, has been blown, facing at right angles to the axis of the tube. On the same side, which in use becomes the upper side, a smaller hole not less than 6 or 7 mm. diameter, is blown in the tube at a point half an inch from the bulb and below this the tube is drawn out to a narrower "tail" about half an inch long, bent a little so as to rest against the lower side of the test tube. Any liquid collecting in this funnel runs down into the tail and through the opening in this, back into the test tubes, and although this hole at once becomes stopped by a drop of liquid, gases have always free exit by the opening on the upper side. The larger outer opening being at right angles insures that even if a small drop were accidentally shot through the stem of the funnel, it would strike the side of the bulb and run back. The shape of the funnel allows of its being rinsed out easily, with a few drops of water, outside and in.

Digestion having been effected in the test tube and the acid diluted with not more than 6 or 8 cc. of water, including that used to rinse the funnel, the whole is poured into a distillation flask of special design, and of such

a size that the whole of the ammonia vapor can be driven over with 10 cc. of water or less. This consisted of a small flask with a bulb holding about 25 cc. and a neck about eight inches long, with an inner up-turned tube as a trap, sealed in, where the side tube was attached to the neck. The latter tube is bent down at right angles and has a small oval bulb just below the bend, from which it tapers down to a long, narrow point, which was inserted in a cork fitted into the mouth of a  $6 \times \frac{3}{4}$  in. test tube. This cork was also fitted with an exit tube bent at right angles; a small funnel with a narrow capillary stem reaching down to the bottom of the tube passed through the cork closing the neck of the flask.

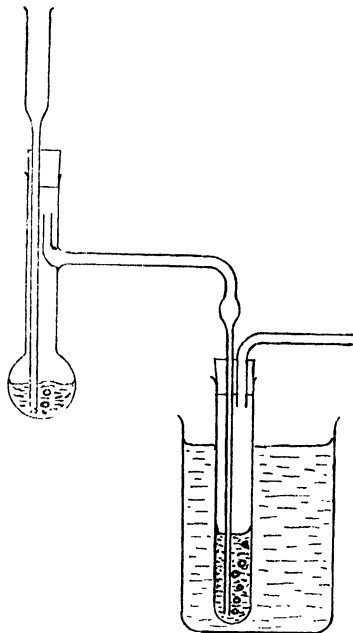


Fig. 5.

Having rinsed out the digestion tube into the flask with not more than 5 cc. of water in two small quantities, a measured quantity of strong caustic soda (2.5 cc. of a nearly saturated solution) which had been found to be slightly more than enough to neutralize the acid, was added and the liquid, which did not measure over 20 cc., distilled into an accurately measured quantity of 0.02 *N* hydrochloric acid in the test tube, a rather rapid current of air being drawn through the apparatus during the operation, by connecting the exit tube to an air pump. In five minutes after boiling the ammonia has all passed over, except for negligible traces, so that this stage of the operation is very quick and easy. Even where mercury has been used, in which case sodium sulfide is also added before distilling, the rapid air current prevents bumping, provided the funnel dips to the bottom of the flask. Frothing rarely causes trouble and can be instantly controlled by removing the source of heat, when the cooling effect of the air current is rapidly felt. The effectiveness of this rapid distillation, and of the trap in preventing the carrying over of alkaline spray, was demonstrated by experiments with known quantities of 0.02 *N* ammonium chloride.

The following results, with known substances, will show the degree of accuracy attained when bumping was avoided:

Antipyrine, taken 0.0075 g. Nitrogen found 0.0011 g. equivalent to 15%. Theory requires 14.9%.

$\alpha$ -Naphthylamine, taken 0.0092 g. Nitrogen found 0.00087 g. equivalent to 9.4%. Theory requires 9.8%.

Caffeine, taken 0.0066 g. Nitrogen found 0.0085 g. equivalent to 28.0%. Theory requires 28.9%.

While a certain percentage of results vary 1% or more from the theoretical requirements, indicating that the method of digestion is still capable of improvement, the close agreement of most results, when the very small quantities used are considered, indicates the usefulness of the method as a guide to the composition of an unknown substance, where the quantities available are limited.

### Conclusions.

1. The proportion of protein, fat, moisture and ash has been determined in air-dried *Oscillaria prolifica*.

2. A systematic extraction of the alga has been carried on with various solvents and the approximate proportions extracted have been determined.

3. A new form of extraction apparatus suitable for continuous extraction with volatile solvents of large quantities of material, is here described. This consists of a double siphon, so constructed that an intermittent flow is obtained, as in a Soxhlet's apparatus, allowing of the periodic filling and emptying automatically, of an ordinary flask, between two fixed levels, without a tubulure or aperture in the side of the flask.

4. Crystalline and easily identified characteristic substances were not found in any considerable quantity in the alga. A small quantity of a crystalline magnesium salt of an organic acid (possibly caproic) has been obtained.

5. Saponin of characteristic properties was not obtained in appreciable quantities; a glucoside or polysaccharide having physical properties similar to saponin exists in the plant.

6. The bad smell and taste of the decaying alga appears to be due largely to higher acids of the fatty (butyric) series, some of which were separated: indole or skatole from decomposition of the proteins seems also to be present in traces. The fresh alga contains an aromatic compound soluble in petroleum spirit which causes a characteristic odor.

7. The spectra have been determined of various coloring matters from the alga, a "chlorophyll" similar to that of the higher plants and a blue substance soluble in water and in glycerol, with an intense red fluorescence, having properties which indicate that it is either associated with and carried down by the proteins in solution, or itself has similar precipitation properties. This substance, which is believed to be new, and may be allied chemically to the chlorophyll of the alga, has been named "algcyan."

8. The chief carbohydrate in the plant is a pectin-like substance insoluble in water with a great power of forming jelly on heating. It is hydrolyzed with remarkable slowness by boiling with 5% sulfuric acid; the examination of the products indicated the presence of a nonreducing

substance with a high positive rotation, and a reducing sugar with smaller rotation (eventually becoming zero or slightly negative) formed from this by further hydrolysis. A small quantity of a phenyl hydrazine compound was obtained which in the pure state melted at  $217^{\circ}$  (corrected) and contained about 11% of nitrogen: this can not be identified with any known compound.

9. A modification of the details of manipulation of the Kjeldahl method of nitrogen determination has been worked out, allowing of approximate analyses of as little as five to ten milligrams of material, containing about one milligram or less of nitrogen.

Boston, Mass.

## THE POISONOUS PRINCIPLE OF POISON OAK

(*Rhus diversiloba*, T. and G.).

By JAMES B. MCNAIR.

Received December 13, 1915.

**Botanical Similarity between Poison Oak (*Rhus diversiloba*) and Poison Ivy (*Rhus toxicodendron*).** — The difference between *Rhus diversiloba* and *Rhus toxicodendron* is so small that their proper classification forms a bone of contention between botanists. Those botanists that believe in innumerable species are in favor of their separation, while the more conservative are opposed to it. Greene,<sup>1</sup> considers *Rhus diversiloba* "a peculiar type of *toxicodendron* belonging exclusively to the Pacific coast." Engler<sup>2</sup> believes *diversiloba* a sub-species of *toxicodendron*. The only botanical ground for the separation of the two into different species is a slight difference in the shape of their leaflets.<sup>3</sup>

**Is the Poison a Glucoside of Rhamnose, Gallic Acid and Fisetin?—** As far as is known to the writer no work has been published on the chemistry of the poisonous principle of poison oak (*Rhus diversiloba* T. and G.). Because of the very close botanical relationship existing between poison oak and poison ivy (*Rhus toxicodendron*, L.) and because of their identical pharmacological action it has always been held among the medical profession, as well as among botanists, that the poisons were identical. Not only are they similar in pharmacological action, but they are also similar in solubility, rapid oxidation, etc.

In seeking to find out the constitution of the poisonous compound of poison oak the work done on its very closely related plant has been investigated. Perhaps the most recent work is that of Syme, 1906,<sup>4</sup>

<sup>1</sup> Ed. L. Greene, "Leaflets of Botanical Observation and Criticism" (1903-1906), Vol. 1, p. 119.

<sup>2</sup> Candolle, "Monographic Phanerogamarum," Vol. 3, p. 395; Engler und Prantl, "Die Natürlichen Pflanzen-familien," 111-5, p. 168 (1897).

<sup>3</sup> Gray, "Synoptical Flora" (1895-7), Vol. 1, Pt. 1, Fasc. 1-2, p. 382-383.

<sup>4</sup> W. A. Syme, "Some Constituents of Poison Ivy Plant," Johns Hopkins University Dissertation, 1906; Acree and Syme, *Am. Chem. J.*, 36, 303, 316 (1906).

who claims to have found upon a hydrolysis of the poison of *Rhus toxicodendron*, rhamnose, gallic acid and fisetin.

In an attempt to secure on hydrolysis of the poisonous principle of poison oak the same constituents as Syme obtained from poison ivy the writer was unsuccessful. Therefore, it must be concluded that the poison of *Rhus diversiloba* is not a glucoside of rhamnose, gallic acid and fisetin.

While we have not repeated the work on the plant Syme experimented with, it seems strange that such closely related plants should have such widely different poisonous principles. It is true that there is often a slight change in the chemical constitution of glucosides, oils, nitrogenous bases, etc., between plants of the same botanical genus, but it is, indeed, an exception where a wide variance occurs as the results of these experiments would indicate.<sup>1</sup>

Such a difference in the chemical nature of the poisons could hardly be laid to a difference in climate or soil. Poison ivy is found all over Eastern United States as well as in Washington and Oregon. Poison oak is found from the Gulf of California to the Canadian border. Who shall say that it does not endure at least as rigid a climate and surely as mild a one as poison ivy?

Fisetin, gallic acid, and rhamnose, the constituents of Syme's glucoside are found in large quantities in two plants of the botanical genus to which both poison ivy and poison oak belong, viz., *Rhus cotinus*, L.<sup>2</sup> and *Rhus rhodanthema*.<sup>3</sup> It might be supposed from Syme's observations that these species would be poisonous. As a matter of fact, however, neither of these species is poisonous.

*Rhus cotinus* yielded, when analyzed in 1886 by Schmid,<sup>2</sup> a glucoside on water extraction which was called "glycosidgerbsäure des Fisetins" or Fustin tannid. This substance gave, on hydrolysis with alkalis or mineral acids, the same substances which Syme's glucoside contained, viz., fisetin, rhamnose, and gallic acid.

While it cannot be positively denied that some poisonous glucoside may exist which contains fisetin, rhamnose, and gallic acid, yet so far as known there has been no corroboration of Syme's conclusion. All the evidence at hand points towards a nontoxicity of a glucoside of fisetin, gallic acid and rhamnose.

In repeating the work of Syme the writer used gasoline as an extractive material in preference to ether which Syme used. This selection was made because the writer realized that gasoline did not appreciably dissolve rhamnose, gallic acid, tannin, or fisetin, whereas ether does act as a solvent for gallic acid, tannin,<sup>4</sup> and fisetin when combined with

<sup>1</sup> Pictet and Biddle, "The Vegetable Alkaloids," p. 114-115.

<sup>2</sup> Schmid, *Ber.*, 79, 1734 (1886).

<sup>3</sup> Perkin, *J. Chem. Soc.*, 71, 1194 (1897).

<sup>4</sup> Beilstein, *Organische Chemie*.



rhamnose.<sup>1</sup> Besides these things ether dissolves many other interfering substances, e. g., chlorophyl,<sup>2</sup> which gasoline does not.

While both of us worked with a "poisonous tar, wax, or gum," yet there is reason to believe that ours was the purer product. It cannot be denied at present that there may be a poisonous glucoside of fisetin, rhamnose, and gallic acid, but there is certainly strong presumptive evidence that such is not the case. There is not sufficient evidence that the poisonous substance which Syme attempted to decompose was not a complex containing the poisonous body and one or more nontoxic glucosides in addition. These may consist of some combination of fisetin, rhamnose, and gallic acid.

We would suggest, therefore, that the work with *Rhus toxicodendron* be repeated for substantiation and a synthesis be made of the pure poison or poisons. For it seems strange indeed that such closely related plants should have such different poisons.

### Experimental Data.

An attempt to verify the results of Syme's hydrolysis was made by the author with the poison of *Rhus diversiloba*.

The poisonous principle in the following experiment was obtained by extracting *chips* of *limbs* in a Soxhlet apparatus with 86° Baumé gasoline. In other experiments the *leaves* have been used and similar results obtained. The gasoline was evaporated and the black residue pulverized in a glass mortar. The powdered material was placed with two liters of distilled water in a tall glass cylinder. The black substance was insoluble in water and sank to the bottom of the cylinder. It was thoroughly shaken at least once a day for a week, after which time the aqueous portion was decanted. Two liters of fresh distilled water were now added and the shaking process repeated for another week. At the expiration of this time the aqueous liquid was decanted from about 25 g. of the black material, and the liquid was evaporated to dryness. The residue, very small—about 3 mg. per liter—represented the amount of water-soluble constituents in the black material.

The black material was repeatedly extracted with 95% alcohol. The first portions of the alcoholic extract were colored light brownish yellow. The later portions of the extract were light yellow, indicating that the chromatic alcohol soluble material had been nearly all extracted. This poisonous alcoholic extract, which amounted to about 800 cc., was heated on the water bath during working hours for two and one-half days with a solution of 2 g. of concentrated sulfuric acid in 100 cc. water—to hydrolyze the alcohol-soluble material.

<sup>1</sup> Schmid, *Ber.*, 79, 1734 (1886).

<sup>2</sup> Syme, *Loc. cit.*

The alcohol was driven off of the solution at the end of the period of treatment. The colors of the solution were as follows:

Color of alcoholic extract, light brownish yellow; color after addition of acid solution, the same; color of solution after driving off alcohol, the same. When the alcohol was driven off there remained, besides the aqueous solution, a quantity of black tar-like material, insoluble in water.

An alcoholic solution of the tar-like material was extremely poisonous, while the aqueous solution was found to be nonpoisonous when applied to tender skin. *In the aqueous solution* should be Syme's so-called hydrolysis products of the poison ivy, *viz.*, fisetin, gallic acid, and rhamnose, as each of these materials is easily soluble in water.

#### Reactions of the Aqueous Solution.

**Rhamnose**, or any other reducing sugar, was not present for the following reasons:

A portion of the solution which had been neutralized to litmus with a sodium carbonate solution gave a slight turbidity when treated with Fehling's solution. The slightest perceptible amount of copper oxide was precipitated, not enough to be a decisive test for reducing sugars.

A portion of the neutralized and also of the unneutralized solution tested with  $\alpha$ -naphthol<sup>1</sup> gave a negative test for carbohydrates. It was found that when the solution was passed through an ordinary filter paper the test gave positive results; this was due to carbohydrates from the paper.

**Gallic acid** was not present for the following reasons:

When a portion of the unneutralized solution was treated with ferric chloride solution a light brown color was produced, no precipitate. The color was somewhat deeper than the original solution before treatment. When a drop of sodium carbonate solution was added, a precipitate of ferric hydroxide was formed, the solution filtered from the mass was nearly colorless, being slightly yellowish.

**Fisetin** was not present, for when a portion of the aqueous solution was shaken with ethyl acetate no coloring matter was extracted from the solution.

#### Comparison of this Attempted Hydrolysis with the Work of Syme.

No similarly colored solution was formed during the hydrolysis as was mentioned in his work.

No tests indicating gallic acid were obtained by means of ferric chloride as is to be found in the dissertation.

Positive tests for rhamnose or reducing sugars with  $\alpha$ -naphthol and Fehling's solution were not obtained. Especial care was taken in the filtrations throughout to use glass wool instead of filter paper in order that dissolved carbohydrates from the paper would not interfere with the test for rhamnose.

<sup>1</sup> Browne, "Handbook of Sugar Analysis," p. 341.

The hydrolysis did not liberate fisetin. This was indicated by the fact that ethyl acetate shaken with the aqueous solution did not extract coloring matter from the solution.

### No Optical Activity.

A gasoline solution of the poison, the aqueous solution of possible hydrolytic products, as well as an ethyl acetate solution of the poisonous hydrolytic residue, exhibited *no* evidences of optical activity when observed through a decimeter tube in a triple field saccharimeter.<sup>1</sup> While this does not positively prove the absence of an asymmetric carbon atom, or rhamnose in the poison, it furnishes strong presumptive evidences in that direction.

From the evidence presented above it is concluded that the poison in *Rhus diversiloba* cannot be hydrolyzed by means of acid into the compounds, rhamnose, gallic acid, and fisetin.

### Summary.

1. *Rhus diversiloba* and *Rhus toxicodendron* are very similar plants; their only botanical difference lies in a slight difference in the shape of their leaflets.

2. The poisonous principle of *Rhus diversiloba* is not a glucoside of rhamnose, fisetin and gallic acid.

3. Syme's conclusion that the poison of *Rhus toxicodendron* is a glucoside of fisetin, rhamnose, and gallic acid should be repeated for substantiation for:

(a) It seems strange that two such closely related plants botanically should have such widely different poisons chemically.

(b) All three of the so-called constituents of the poison are found in two nonpoisonous species of *Rhus*.

(c) The natural glucoside of fisetin, rhamnose and gallic acid is non-toxic.

(d) There is not sufficient evidence that a poisonous substance which Syme attempted to decompose was not a complex containing a poisonous body to one or more nontoxic glucosides in addition.

I am indebted to Professors H. C. Biddle and T. Brailsford Robertson for their advice throughout the investigation.

BERKELEY, CALIF.

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## ON THE CONSTITUENTS OF POISON IVY (*Rhus toxicodendron*).

BY S. F. ACREE.

Received March 22, 1916.

The interesting article presented in the preceding pages was kindly referred to me by the author for the publication of a simultaneous note. As Dr. Syme died several years ago and his note-books are not available,

<sup>1</sup> Made by Hantz Schmidt Haensch, Berlin, Germany.

and the busy life makes us forget the details of work finished ten years before, the writer can give only a general statement regarding the preceding note by McNair. This article has been referred to him.

Two points in McNair's paper will be discussed: Namely, (1) the logic and, (2) the facts, imperfections in either of which lead, save by accident, to wrong conclusions. Syme had considerable knowledge of this difficult plant work and was peculiarly adapted to this kind of problem. He worked on the *ether extract* of the *leaves and flowers* of *Rhus toxicodendron*, whereas McNair worked on the *gasoline extract* of the *limbs* of *another species*, *Rhus diversiloba*, and, as *might* be expected, secured *different results*. He therefore concluded that *Syme's work* is wrong. The only other comment to be added is that McNair may not have given sufficient weight to the well-known fact that the botanical differences in species may often be detected only with difficulty whereas the chemical differences may differ widely. This phase of the work has been discussed a number of times, especially in an illuminating article by Schorger<sup>1</sup> to whom I am indebted for the following résumé.

It is well known that the same plant yields very different volatile oils in different localities having different soils, moisture conditions, and climates. The Lavender plant (*Lavandula vera*) of France gives an oil containing 40 to 42% of esters, whereas in England the same species gives an oil whose ester content never exceeds 10%. The fennel oil produced in Saxony, Galicia, and Moravia, contains fenchone, which is entirely absent in the Macedonian product. Clover<sup>2</sup> and Bacon<sup>3</sup> showed that different trees of the species *Canarium luzonicum* A. Gray gave resins which yielded oils consisting either of pure terpinene, limonene, or phellandrene. Bourquelot and Fichtenholz<sup>4</sup> found the glucoside arbutine in the leaves of *Pyrus communis* but none could be detected in the leaves of *Cydonia vulgaris* Pers., *Malus communis* Link., *Sorbus aucuparia* L., or *S. torminalis* Crantz, all of which were formerly classed as *Pyrus*.

Another very interesting case is a set of the oils obtained by Schorger from Jeffrey pine, western yellow pine, and the "cross variety" pine, which resemble each other so closely that it is difficult to tell them apart by botanical methods. The oil from the Jeffrey pine boils at about 98° and contains 95% of heptane. The oil from the typical western yellow pine (*P. ponderosa*) boils at 164° and contains no heptane and yields about 65% of  $\beta$ -pinene. The "cross variety" of the western yellow pine boils at 165° and contains  $\beta$ -pinene, and limonene in some cases. The

<sup>1</sup> "Chemistry as an Aid in the Identification of Species," *Proc. Soc. Am. Forest.*, **11**, 33 (1916).

<sup>2</sup> *Phil. J. Sci.*, **2A**, 1 (1907).

<sup>3</sup> *Ibid.*, **4A**, 93 (1909).

<sup>4</sup> *J. pharm. chim.*, **VII**, 3, 5 (1911).

"bastard" pine boils at  $156^{\circ}$  and contains no heptane but about 65% of  $\alpha$ -pinene. The western yellow pine (*P. ponderosa scopulorum*) of Arizona boils at  $157^{\circ}$  and contains no heptane but about 65% of  $\alpha$ -pinene. The optical rotations of these substances vary in a similar way.

Schorger has discovered some other facts of great interest in this connection. The oleoresin from both *P. jeffreyi* and *P. sabiniana*<sup>1</sup> give heptane on distillation. The oil distilled from the needles and twigs of *P. sabiniana* was found to contain only 3% of heptane, the remainder consisting of *terpenes*.<sup>2</sup> This small amount of heptane may, doubtless, be that which occurred in the woody portion of the twigs. *Many other cases are known in which the leaves contain compounds not found in the bodywood, bark, or roots of the same tree, and vice versa.*

This observation and the results given above show beyond question that the phytochemical processes occurring in the needles and in the wood of these conifers are entirely different. This being the case it would be dangerous to assume that the poison occurring in the *leaves and flowers* of *Rhus toxicodendron* should be found in the *bodywood* of this plant and certainly it is entirely inadmissible to assume that this same poison, or the same nontoxic constituents, should be found in the *limbs* of an entirely different species, *Rhus diversiloba*.

McNair's discussion of the solubilities of complex glucosides and their relation to the solubilities of the components, as well as his reasoning on the relation of the toxicity of a complex organic compound to the toxicity of the constituents, or *vice versa*, will find many opponents among the pharmacologists and plant chemists. Any good book, such as Fraenkel's "Arzneimittelsynthese," gives numberless illustrations to show that the general relationships assumed by McNair can not hold. Derivatives of saccharin lose the sweet taste. The local anesthetic cocaine is made up of a combination of ecgonine, benzoic acid and methyl alcohol, no one of which has the same action as the cocaine. The examples could be multiplied indefinitely, as I am assured by my friends, Loevenhart and Kremers.

Coming to the discussion of (2) Syme's *facts*, we note again that because McNair *failed* to find gallic acid, fisetin and rhamnose as free or combined constituents of the *gasoline extract* of the *limbs* of *Rhus diversiloba* he concludes that Syme could not have found them in the *ether extract* of the *leaves and flowers* of another species *Rhus toxicodendron*.

McNair criticizes Syme's work on the hydrolysis products of the poisonous tar or wax after simply making a few negative color tests. After noting that McNair himself did not isolate anything more crystalline than a "dark liquid mystery," which still remains so, let us review

<sup>1</sup> Bull. 119 Forest Service; *J. Ind. Eng. Chem.*, 5, 971 (1913).

<sup>2</sup> *J. Ind. Eng. Chem.*, 7, 24 (1915).

what Syme actually obtained in the crystalline state. From the aqueous extract of the total poisonous tar Syme obtained crystalline potassium, barium and sodium salts and crystalline gallic acid, melting point  $230^{\circ}$ , and converted it into the crystalline ethyl ester, which melted at  $156-9^{\circ}$ , whether alone or mixed with the ethyl ester prepared from Kahlbaum's gallic acid. He then subjected the gallic acid to the characteristic color and other tests discussed in his dissertation. The most concentrated "poisonous tar, gum or wax," was called the "poison" for brevity, but was obviously never considered to be "crystalline" and pure. This substance, on hydrolysis, gave the same characteristic color and other tests for gallic acid, but the amount of "poison" available was too small to attempt to isolate crystals and it was used chiefly for the more valuable toxicity and other tests.

Turning to the dyestuff, fisetin, which McNair could not find in another species, we note that Dr. Syme did isolate crystalline fisetin from the total tar, studied its color reactions and even decomposed two grams of it into phloroglucinol and protocathechuic acid. Syme was already familiar with fisetin and I believe had samples for comparison. As stated above, the amount of the most concentrated "poison" was too small to allow Syme to isolate crystalline fisetin from its hydrolysis products, but he obtained the same characteristic color and other tests found for his crystalline fisetin.

Coming to rhamnose we found that Syme discussed fully the difficulties of obtaining this sugar, as indeed most sugars, in the crystalline state. He had to be content, therefore, with characteristic color and other tests worked out for crystalline rhamnose, including of course the conversion into methyl furfural.<sup>1</sup> Of course a number of the methyl pentoses discovered since that time give a number of similar tests.

As stated above, the "poison" was a tar, wax or gum, and Warren believes that this "poison" may have been a complex mixture containing the pure poison or poisons and one or more nontoxic glucosides which can yield the gallic acid, fisetin and rhamnose. Warren and McNair then agree with Syme's Paragraph 3, p. 563, *J. Biol. Chem.*, Vol. II. "In this experiment, gallic acid and fisetin and probably sugar were formed by decomposition of the poisonous gum with acetic acid, the acid found in the plant by Pfaff. The presence of free gallic acid, fisetin, and rhamnose in the plant can be explained by the natural *hydrolysis of a complex gum or tar or a constituent thereof* (italics new). The poisonous property is lost in the general rearrangement which takes place during hydrolysis." This conclusion was so obvious that it never occurred to Syme or the writer that any other conclusion could be drawn from the work. Any organic chemist knows that such a tar is a mixture, and Syme never for a

<sup>1</sup> Dissertation, pages 23-25.

moment desired to word his articles in such a way that the reader would be left under the impression that a "pure poison" could be obtained in this way. The whole object of this work was to isolate the poison in some fraction or fractions, and study these fractions with the view (1) of measuring the toxicity and finding a method ( $\text{KMnO}_4$ ) for curing the wounds, and with the aims (2) of isolating and synthesizing the real poison or poisons. The work was discontinued because the very small amount of "poison" in the \$100 worth of "total poison or tar" available made the further prosecution of the problem appear too expensive. We should indeed be glad to see anyone with the necessary funds continue this research and synthesize the pure poison or poisons. Success in this direction would mean much toward the solution of a problem which causes a great deal of human suffering.

### Summary.

1. McNair's reasoning that the limbs of *Rhus diversiloba* should contain the same toxic and nontoxic constituents found in the leaves and flowers of another species, *Rhus toxicodendron*, in another locality and climate is against all the well-known evidence because:

(a) The botanical differences in species may often be detected only with difficulty while the chemical constituents may vary widely.

(b) The same species gives different substances in different localities and climates.

(c) The constituents found in the leaves of a given species are generally *not* identical with those found in the limbs of the same plant, much less of a different species under different conditions.

2. It is highly probable that Syme's "purified poisonous tar, gum or wax" was a mixture of toxic and nontoxic materials. Syme's "purified" the material as far as possible and when it gave out suspended the work on account of the expense. Although his description of the "purified poisonous tar, gum, or wax" and its reactions was in some places perhaps confusing, Syme did not believe that his "purified poison" was not a mixture. It is highly desirable to have the studies on all these toxic plants continued.

DEPARTMENT OF CHEMISTRY OF FOREST PRODUCTS,  
UNIVERSITY OF WISCONSIN, MADISON.

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[FROM THE ANIMAL HUSBANDRY DEPARTMENT OF THE UNIVERSITY OF ILLINOIS.]

## THE NONPROTEIN NITROGENOUS CONSTITUENTS OF FEEDINGSTUFFS.

BY H. S. GRINDLEY AND H. C. ECKSTEIN.

Received May 25, 1916.

When the Van Slyke method for the determination of the chemical groups characteristic of the different amino acids of proteins was first

proposed as a method for the estimation of the free and the combined amino acids and the free and the combined amides of feedingstuffs,<sup>1</sup> it was realized that it would be necessary, in order to establish the accuracy of the method, to demonstrate that the nonprotein nitrogenous constituents of feedingstuffs do not lead to inaccurate experimental results or to results that falsify the interpretation of the experimental data so obtained. The investigation here reported was undertaken as a necessary step in this direction. The preliminary results of this work were reported at the New Orleans meeting of this Society.<sup>2</sup> Since that time Hart and Bentley<sup>3</sup> have published a paper relating to this same subject.

Briefly stated, the method finally adopted for the work here reported was as follows:

Ten to twenty-five grams of the feedingstuff, placed upon a four-inch Büchner funnel, were washed repeatedly with cold ammonia-free water until the filtrate measured about 2400 cc. The extract was diluted to 2500 cc.

(a) **The Total Soluble Nitrogen** was determined in 200 cc. portions of the extract in duplicate.

(b) **The Free Ammonia** was determined in a 500 cc. portion of the extract by the Van Slyke vacuum method.

The native-proteins were separated in a 1250 cc. portion of this extract by heating it to boiling and by adding, drop by drop, while constantly stirring 7.5 cc. of colloidal ferric hydroxide<sup>4</sup> (containing 5% of  $\text{Fe}_2\text{O}_3$ ). The solution was then boiled for one minute and 1.0 cc. of a solution of crystallized magnesium sulfate (made by dissolving  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  in an equal weight of water), was added to coagulate the excess of colloidal ferric hydroxide. The solution was again boiled for one minute. After standing overnight, the solution was filtered through folded filters and the precipitate was thoroughly washed with hot water. The filtrate and washings after being diluted to 1500 cc. were used for the following determinations:

(c) **The Total Nitrogen** not precipitated by the colloidal ferric hydroxide was determined in duplicate in 200 cc. portions.

(d) **The Free Ammonia** was determined in one portion of 500 cc. by the Van Slyke vacuum method.

(e) **The Free Amino-Acid Nitrogen** was determined by slightly acidifying the residual mixture left in the distilling flask from the above determination in (d) with hydrochloric acid, filtering and washing. The filtrate and washings were evaporated in a porcelain dish on the steam

<sup>1</sup> THIS JOURNAL, 37, 1778 (1915); 37, 2762 (1915).

<sup>2</sup> See *Science*, 42, 70 (1915) for abstract of paper.

<sup>3</sup> *J. Biol. Chem.*, 22, 477 (1915).

<sup>4</sup> Merck's.



bath to about 15 cc. The concentrated solution was washed into a 25 cc. measuring flask and diluted to the mark. The amino-acid nitrogen was determined in duplicate in 10 cc. portions of this solution by the Van Slyke nitrous acid method.

(f) **The Free and Combined Acid-Amide Nitrogen** were determined in a 500 cc. portion of the solution by adding enough of concentrated hydrochloric acid to give a concentration of 20% and then boiling under a reflux condenser for 12 hours. The excess of hydrochloric acid was removed by evaporation *in vacuo* and the ammonia determined by the Van Slyke vacuum method. One-half of the weight of the free ammonia nitrogen determined above in (b) subtracted from the weight of the ammonia nitrogen obtained in this determination gave the weight of the free and combined acid-amide nitrogen in one-half the quantity of the feedingstuff originally taken for the analysis. The free ammonia nitrogen as determined in the original water extract was considered more accurate than the corresponding determination in the filtrate from the colloidal iron precipitation, as the heating of the solution during the latter precipitation, clearly hydrolyzed, in part, the free acid amides present with the liberation of ammonia.

(g) **The Humin Nitrogen**, which was formed in the above determination by boiling the aqueous extract of the feedingstuffs with 20% hydrochloric acid for 12 hours, was filtered off and washed as per the Van Slyke method. The nitrogen in the humin precipitate was determined by the Kjeldahl method.

(h) **The Combined Amino-Acid Nitrogen** was determined by slightly acidifying the filtrate and washings from the above determination in (g) and then evaporating the resulting solution in a porcelain dish on the steam bath to about 30 cc. The concentrated solution was washed into a 50 cc. measuring flask and diluted to the mark. The amino-acid nitrogen was determined in duplicate in 10 cc. portions of this solution by the Van Slyke nitrous acid method. The free amino-acid nitrogen determined above in (e) subtracted from the free and combined amino-acid nitrogen obtained in this determination gave the combined amino-acid nitrogen.

(i) **The Residual Soluble Nitrogen**, which did not respond to any of the above tests, was obtained by subtracting the sum of one-half of the free ammonia nitrogen obtained in (b), the free amino-acid nitrogen obtained in (e), the free and combined acid-amide nitrogen obtained in (f), the humin nitrogen obtained in (g), and the combined amino-acid nitrogen obtained in (h) from the total nitrogen not precipitated by colloidal iron hydroxide obtained in (c).

It is possible that some of the humin nitrogen has its origin in the free amino-acid nitrogen. If this is true, then the residual soluble nitrogen

would necessarily be increased to an equivalent extent. At present, it is impossible to determine how much of the humin nitrogen comes from the free amino-acid nitrogen, and how much of it comes from the combined amino-acid nitrogen.

Much difficulty was experienced in obtaining a complete extraction of the food material with cold water. By the method described above the total nitrogen not precipitated by colloidal ferric hydroxide in a second extract following the first, and measuring 1000 cc., was reduced to less than 0.6% of the total nitrogen present in the alfalfa hay; to less than 0.5% of the total nitrogen of timothy hay; to less than 0.3% of the total nitrogen of the corn; and to less than 0.07% of the total nitrogen of the blood meal.

The use of colloidal ferric hydroxide for the separation of the proteins from the nonproteins was suggested by the recent use of this reagent for the separation of proteins from blood, milk, and partially digested proteins by Wolff,<sup>1</sup> Hill,<sup>2</sup> and Van Slyke,<sup>3</sup> *et al.*, Van Slyke, Vinograd-Villchur and Losee<sup>3</sup> say: "In experiments on Witte peptone and partially digested protein to be published later we have found, furthermore, that colloidal ferric hydrate not only lets all the amino acids go through

TABLE I.—THE NONPROTEIN NITROGENOUS CONSTITUENTS OF FEEDINGSTUFFS.

Results Expressed in Per Cent. of the Total Nitrogen of the Feedingstuffs.

Feed.	In the original extract.			In the filtrate from the colloidal iron precipitate.						
	Total nitrogen.	Free ammonia nitrogen.	Nitrogen precipitated by colloidal iron.	Total nitrogen.	Humin nitrogen.	Free amino-acid nitrogen.	Free and combined amide nitrogen.	Combined amino-acid nitrogen.	Residual soluble nitrogen.	
Alfalfa hay.....	28.58	1.07	11.07	17.51	1.40	5.08	3.40	3.10	3.46	
Alfalfa hay.....	28.21	1.15	10.63	17.58	1.48	5.00	3.29	3.15	3.51	
Average.....	28.40	1.11	10.85	17.55	1.44	5.04	3.35	3.13	3.49	
Timothy hay.....	23.58	1.44	8.38	15.20	2.67	4.82	2.67	1.19	2.41	
Timothy hay.....	23.92	1.49	8.27	15.65	2.70	4.84	2.60	1.14	2.88	
Average.....	23.75	1.47	8.33	15.43	2.69	4.83	2.64	1.17	2.65	
Blood meal.....	2.33	0.19	0.49	1.84	0.04	0.58	0.47	0.48	0.08	
Blood meal.....	2.33	0.14	0.43	1.90	0.05	0.57	0.49	0.52	0.13	
Average.....	2.33	0.17	0.46	1.87	0.05	0.58	0.48	0.50	0.11	
Corn.....	7.17	0.66	1.55	5.62	0.24	2.16	1.04	0.57	0.95	
Corn.....	7.74	0.70	2.06	5.68	0.36	2.17	1.08	0.51	0.86	
Average.....	7.46	0.68	1.81	5.65	0.30	2.17	1.06	0.54	0.91	
Clover hay.....	16.50	1.99	2.29	14.21	1.77	4.32	1.40	0.19	4.54	
Clover hay.....	16.60	1.98	2.37	14.23	1.78	4.42	1.18	0.29	4.58	
Average.....	16.55	1.99	2.33	14.22	1.78	4.37	1.29	0.24	4.56	

<sup>1</sup> *J. Physiol.*, 49, 89 (1915).

<sup>2</sup> *J. Biol. Chem.*, 20, 175 (1915).

<sup>3</sup> *Ibid.*, 23, 381 (1915).

TABLE II.—THE NONPROTEIN NITROGENOUS CONSTITUENTS OF FEEDINGSTUFFS.

Results Expressed in Per Cent. of the Feedingstuffs.

Feed.	In the original extract.			In the filtrate from the colloidal iron precipitate.					
	Total nitrogen.	Free ammonia nitrogen.	Nitrogen precipitated by colloidal iron.	Total nitrogen.	Humin nitrogen.	Free amino-acid nitrogen.	Free and combined acid-amide nitrogen.	Combined amino-acid nitrogen.	Residual soluble nitrogen.
Alfalfa hay.....	0.751	0.028	0.290	0.461	0.037	0.134	0.089	0.081	0.092
Alfalfa hay.....	0.741	0.030	0.279	0.462	0.039	0.131	0.086	0.083	0.093
Average.....	0.746	0.029	0.285	0.462	0.038	0.133	0.088	0.082	0.093
Timothy hay....	0.202	0.012	0.072	0.130	0.023	0.042	0.023	0.010	0.020
Timothy hay....	0.205	0.013	0.071	0.134	0.023	0.042	0.022	0.008	0.026
Average.....	0.204	0.013	0.072	0.132	0.023	0.042	0.023	0.009	0.023
Blood meal.....	0.327	0.026	0.069	0.258	0.005	0.082	0.065	0.068	0.012
Blood meal.....	0.326	0.019	0.061	0.265	0.007	0.079	0.069	0.073	0.018
Average.....	0.327	0.023	0.065	0.262	0.006	0.081	0.067	0.071	0.015
Corn.....	0.103	0.009	0.022	0.081	0.004	0.031	0.015	0.008	0.014
Corn.....	0.111	0.010	0.029	0.082	0.005	0.031	0.015	0.006	0.015
Average.....	0.107	0.010	0.026	0.082	0.005	0.031	0.015	0.007	0.015
Clover hay.....	0.330	0.040	0.045	0.285	0.035	0.090	0.028	0.004	0.088
Clover hay.....	0.332	0.040	0.047	0.285	0.036	0.091	0.024	0.006	0.088
Average.....	0.331	0.040	0.046	0.285	0.036	0.091	0.026	0.005	0.088

TABLE III.—THE NONPROTEIN NITROGENOUS CONSTITUENTS OF FEEDINGSTUFFS.

Results Expressed in Per Cent. of the Total Soluble Nitrogen not Precipitated by Colloidal Ferric Hydroxide.

Feed.	Total nitrogen.	Free ammonia nitrogen.	Humin nitrogen.	Free amino-acid nitrogen.	Free and combined acid-amide nitrogen.	Combined amino-acid nitrogen.	Residual soluble nitrogen.
Alfalfa hay.....	100.00	6.32	8.21	28.72	19.09	17.83	19.89
Timothy hay.....	100.00	9.53	17.43	31.30	17.11	7.58	17.07
Blood meal.....	100.00	9.09	2.67	31.02	25.67	26.74	5.88
Corn.....	100.00	12.04	5.31	38.41	18.76	9.56	16.11
Clover hay.....	100.00	13.99	12.52	30.73	9.07	1.69	32.07

into the filtrate, but that it also precipitates none of the intermediary products up to the albumoses, and none of these except some of complexity but little below that of the original proteins (proportion of amino nitrogen was but 6 to 7% of the total in the precipitated albumoses). As the precipitation of the native proteins themselves is complete, colloidal ferric hydrate appears especially well adapted to our purpose."

The character of the results obtained by the application of this method to the examination of a few feedingstuffs is apparent from the data given in Tables I, II, and III. In Table I, the nonprotein nitrogenous constituents of feedingstuffs are given expressed in per cent. of the total nitrogen of the feedingstuff. In Table II, the nonprotein nitrogenous constituents are expressed in per cent. of the feedingstuff. In Table III, the non-

protein nitrogenous constituents are expressed in per cent. of the total soluble nitrogen not precipitated by colloidal ferric hydroxide.

It is apparent that this method of the determination of the nonprotein nitrogenous constituents of feedingstuffs gives a fairly complete picture of the different forms of nitrogen represented in the so-called nonprotein nitrogenous constituents.

It is also apparent that the nonprotein nitrogenous constituents consist largely of the forms of nitrogen that result from the decomposition of proteins by hydrolysis. In other words, the sum of the amide nitrogen, the humin nitrogen, the free amino-acid nitrogen, the combined amino-acid nitrogen, and the free and combined acid-amide nitrogen represented in the nonprotein nitrogenous constituents form from 80% in the case of alfalfa hay to 94% in case of blood meal, of the nonprotein nitrogen. Further, it is probable that at least 50% of the residual soluble nitrogen not precipitated by colloidal iron represents the nonamino nitrogen present in the free and combined amino acids determined.

It is impossible at present to tell definitely what the remaining 3 to 10% of residual soluble nitrogen, which does not respond to any of the tests here applied, represents. However, it seems quite evident that only a small part, if any, of the nonprotein nitrogenous constituents of foods and feedingstuffs can in any way interfere with the application of the Van Slyke method for the determination of the chemical groups characteristic of the different amino acids of protein to the estimation of the free and combined amino acids and amides of feedingstuffs.

It is also evident that the so-called amide nitrogen of feedingstuffs is largely composed of free amino acids and peptide linkings. The nitrogen in these latter forms including the humin nitrogen constitute from 53 to 63% of the water-soluble nitrogen not precipitated by colloidal ferric hydroxide. Hart and Bentley<sup>1</sup> by the use of their method, which differs entirely from the method we here propose, reported 50 to 70% of the water-soluble nitrogen of immature and mature plants, that was not precipitated by boiling the slightly acidified extracts, as free amino acids and peptide linkings.

The free and combined acid-amide nitrogen varied from 17.11 to 25.67% of the soluble nitrogen not precipitated by colloidal ferric hydroxide. Hart and Bentley found the "free acid-amide nitrogen" by their method to be relatively small, seldom exceeding 20% of the water-soluble nitrogen, and more often being below 10%. Our results which represent the free and the combined acid-amide nitrogen are not directly comparable with those of Hart and Bentley which they considered to represent only the free acid-amide nitrogen. However, it does not seem probable, that the results they obtained for this determination represent merely free acid-

<sup>1</sup> *J. Biol. Chem.*, 22, 477 (1915).

amide nitrogen, for it is a well-known fact that proteins and peptide linkings very readily yield ammonia when boiled with 20% hydrochloric acid.

In the work here reported the free ammonia nitrogen varied from 6.33 to 12.04% of the water-soluble nitrogen not precipitated by colloidal iron. Hart and Bentley found by their method that the free ammonia nitrogen of immature and mature plants rarely exceeded 5% of the water-soluble nitrogen, and in some instances was wholly absent. Their low results for ammonia were probably due to the direct extraction of the food materials with *hot* water. We have confirmed the results of Hart and Bentley that an extract of alfalfa hay prepared with boiling water contains no free ammonia, or at least only a slight trace. On the other hand, as shown in the Table III, a cold water extract of alfalfa hay contained 6.33% of its total soluble nitrogen not precipitated by colloidal iron, in the form of free ammonia. Further, an extract of alfalfa hay prepared by hot water slightly acidified (0.185% hydrochloric acid), contained 4.44% of its total soluble nitrogen, not precipitated by colloidal iron, as free ammonia. A water extract of alfalfa hay is distinctly alkaline to litmus paper.

Further studies to determine the amount and the nature of the nonprotein nitrogenous constituents of feedingstuffs are now under way in this laboratory.

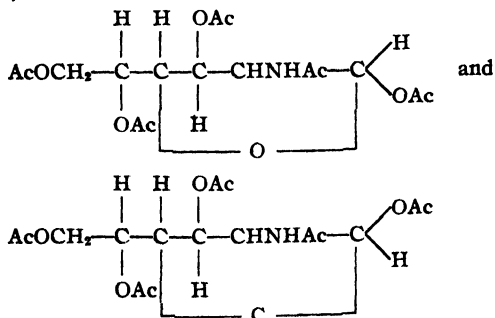
URBANA, ILL.

## THE ISOMERIC PENTACETATES OF GLUCOSAMINE AND OF CHONDROSAMINE.<sup>1</sup>

BY C. S. HUDSON AND J. K. DALE.

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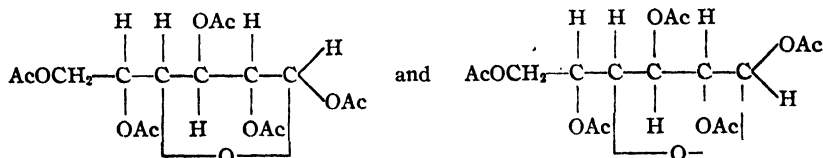
Two isomeric pentacetyl derivatives of glucosamine have been described by Lobry de Bruyn and Van Ekenstein.<sup>2</sup> If these compounds have the isomeric structures,



<sup>1</sup> Contribution from the Carbohydrate Laboratory, Bureau of Chemistry, United States Department of Agriculture.

<sup>2</sup> *Rev. trav. chim.*, 18, 83 (1899).

the molecular rotations of the substances may be expressed by the quantity  $(A + B)$  for one form and  $(-A + B)$  for the other, in accordance with considerations advanced by one of us,<sup>1</sup> and more recently developed in connection with the acetyl derivatives of the sugars.<sup>2</sup> The quantity  $A$  represents the rotation which is due to the end asymmetric carbon atom and  $B$  denotes the rotation due to the remainder of the molecule. In a similar manner the molecular rotations of the alpha and beta forms of glucose pentacetate,



may be written  $(A + B')$  and  $(-A + B')$  where  $B'$  is of different value from  $B$  on account of the dissimilarity of the glucose and glucosamine chains. The difference between these values for the alpha and beta glucosamine pentacetates is  $2A$  and the corresponding difference for the glucose pentacetates is also  $2A$ . The deduction is drawn that the difference between the molecular rotations of the glucosamine pentacetates is equal to that of the glucose pentacetates. Lobry de Bruyn and Van Ekenstein found the specific rotation in chloroform solution of the more soluble glucosamine pentacetate to be  $+86.5^\circ$  and the less soluble form to be optically inactive, thus a molecular<sup>3</sup> rotation difference of  $+33,600$ . The similar difference for the glucose pentacetates we have found to be  $+38,100$ .<sup>4</sup> The disagreement amounts to 4,500 or about  $11.5^\circ$  in specific rotation. This considerable divergence suggested to us that the specific rotation of one or both of the glucosamine pentacetates might be in error due to an incomplete separation of the isomers. Accordingly, the preparation and purification of these compounds was undertaken for a re-determination of their specific rotations. We have found for the more soluble glucosamine pentacetate, which we will call alpha because it is more dextrorotatory than the other isomer,  $[\alpha]_D^{20} = +93.2^\circ$ , instead of  $+86.5^\circ$ , and for the less soluble pentacetate, the beta form,  $[\alpha]_D^{20} = +1.2^\circ$ , instead of optical inactivity. These values correspond to a molecular rotation difference of  $+35,800$  which is 2,300 less than the difference for the glucose pentacetates, a disagreement of about  $6^\circ$  in specific rotation. Although this difference is more than the uncertainty of the mea-

<sup>1</sup> Hudson, *THIS JOURNAL*, **31**, 66 (1909).

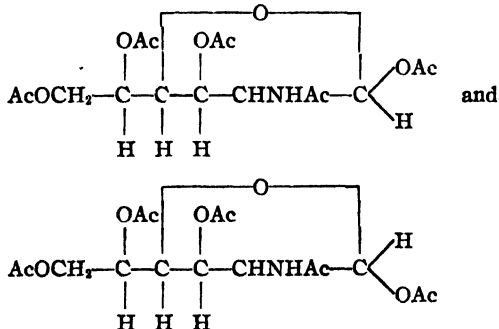
<sup>2</sup> *Ibid.*, **37**, 1264, 1270, 1276, 1280, 1589, 1591, 2748 (1915).

<sup>3</sup> The molecular weights used are 389 for glucosamine pentacetate and 390 for glucose pentacetate.

<sup>4</sup> *THIS JOURNAL*, **37**, 1264 (1915).

surements, on the other hand, the agreement with the theory is close enough to justify the nomenclature we have adopted for the two substances.<sup>1</sup>

**The Isomeric Pentacetates of Chondrosamine.**—Chondrosamine hydrochloride, prepared by Levene and LaForge,<sup>2</sup> is isomeric with glucosamine hydrochloride. The existence of two pentacetates of glucosamine suggested the existence of two similar derivatives of chondrosamine. Both of these compounds have been prepared as described in detail farther on and their specific rotations in chloroform carefully measured. Since chondrosamine hydrochloride has been shown to be the hydrochloric acid salt of either *l*-allose- or *l*-altrose-amine,<sup>3</sup> the structures of its pentacetyl derivatives will be, for one form,



for the other. The end asymmetrical carbon atom in these compounds has the same configuration as in glucosamine pentacetate and glucose pentacetate, but the remainder of the molecule is different, hence the molecular rotations of the alpha and beta forms may be written  $(-A + B'')$  and  $(A + B'')$ .<sup>4</sup> The difference is  $-2A$ , identical with the quantity that was found for the glucosamine pentacetates and the glucose pentacetates, but opposite in sign, hence the difference of the molecular rotations of the chondrosamine pentacetates should be equal and opposite to that of the glucosamine pentacetates and of the glucose pentacetates. In Table I is given the specific rotation of each of these compounds with the corresponding molecular rotation and the differences in molecular rotation.

<sup>1</sup> Lobry de Bruyn and Van Ekenstein named these compounds in the opposite sense, the less soluble form, alpha, and the more soluble form, beta, their reason seeming to be that the less soluble isomer was obtained first.

<sup>2</sup> *J. Biol. Chem.*, **18**, 126 (1914).

<sup>3</sup> Levene and LaForge, *J. Biol. Chem.*, **20**, 433 (1915).

<sup>4</sup> Since chondrosamine is genetically related to *l*-glucose, the lower rotating pentacetyl derivative is to be named the alpha form and the higher rotating isomer the beta. See *THIS JOURNAL*, **31**, 66 (1909).

TABLE I.

Substance.	$[\alpha]_D^{20}$ <sup>1</sup>	Molecular rotation.	Difference.
$\alpha$ -Glucosamine pentacetate.....	+ 93.5°	+36,400 = +A + B	35,930 = 2A
$\beta$ -Glucosamine pentacetate.....	+ 1.2°	+ 470 = -A + B	
$\alpha$ -Chondrosamine pentacetate.....	+ 10.5°	+ 4,100 = -A + B"	-35,400 = -2A
$\beta$ -Chondrosamine pentacetate....	+101.3°	+39,500 = +A + B"	
$\alpha$ -Glucose pentacetate.....	+101.6°	+39,600 = +A + B'	38,100 = 2A
$\beta$ -Glucose pentacetate.....	+ 3.8°	+ 1,500 = -A + B'	

The values of 2A for the acetylated amino sugars agree closely with each other, the disagreement corresponding to only about 1.5° in specific rotation. With the glucose pentacetates the agreement is not so good, the divergence amounting to about 6° in specific rotation in one case and 7.5° in the other. These facts seem to indicate that the nature of the groups on the chain have in this case a definite, though small, influence upon the rotation of the end asymmetrical carbon atom.

### Experimental.

**Preparation of Glucosamine Hydrochloride and the  $\alpha$ - and  $\beta$ -Glucosamine Pentacetates.**—Glucosamine hydrochloride was prepared both from lobster shells and crab shells. Both materials gave a good yield of the amino sugar, but crab shells had the advantage in being cleaner and easier to work with. The lobster shells required a preliminary treatment with caustic soda whereas the crab shells were immediately digested with 5% HCl. This treatment was continued with one or two renewals of the acid until the evolution of CO<sub>2</sub> had ceased. The softened shells were washed and boiled with concentrated HCl, more acid being added from time to time until the shells were completely decomposed and the whole mass had become a thick, black mush. This was diluted with three times its volume of water, warmed with the addition of some active decolorizing carbon such as "eponite" or "norit" and filtered. The filtrate, which was clear and colorless, on evaporation under diminished pressure, crystallized in the flask. The crystals were filtered off and washed with 75% alcohol. The product thus prepared was nearly pure hydrochloride of glucosamine.

The acetylation of this compound was carried out with sodium acetate and acetic anhydride according to the directions of Lobry de Bruyn and Van Ekenstein.<sup>2</sup> The less soluble isomer, the  $\beta$ -pentacetate, was recrystallized from alcohol until its specific rotation became constant. The pure substance melted at 118–189° corr. With chloroform as solvent 1.0828 g. of this compound per 25 cc. of the solution gave a reading to the right +0.1° in a two decimeter tube with sodium light, hence

<sup>1</sup> All specific rotation measurements were made in chloroform (*chloroformum purificatum*, U. S. P.) solution.

<sup>2</sup> *Loc. cit.*



$[\alpha]_{20}^D = +1.2^\circ$ . After another recrystallization a duplicate measurement in which 1.1092 g. of the compound were used gave  $[\alpha]_{20}^D = +1.3^\circ$ .

An acetyl determination made by boiling 0.3034 g. of the acetate with 20%  $\text{H}_2\text{SO}_4$ , distilling off the acetic acid into a flask and titrating with 0.1 N NaOH gave 77.13% acetic acid, which agrees with the theoretical value 77.12% for pentacetyl glucosamine.

The more soluble isomer, the alpha pentacetate, was recrystallized from water, then from alcohol and then from ether until its specific rotation became constant. The pure compound melted at  $139\text{--}140^\circ$  corr. With chloroform as solvent, 1.2762 g. gave a reading to the right  $+9.55^\circ$  in a two decimeter tube with sodium light, hence  $[\alpha]_{20}^D = +93.5^\circ$ . A duplicate measurement using 1.0561 g. of the substance gave  $[\alpha]_{23}^D = +93.3^\circ$ .

An acetyl determination gave 77.25% acetic acid.

**Preparation of  $\alpha$ -Chondrosamine Pentacetate.**—The first supply of chondrosamine hydrochloride was obtained through the courtesy of Dr. P. A. Levene, of the Rockefeller Institute for Medical Research. A later supply was prepared by Mr. E. P. Clark, of this laboratory, according to the directions of Levene and LaForge.<sup>1</sup>

The acetylation of this amino sugar was easily accomplished. To 80 cc. of acetic anhydride in which had been dissolved twelve grams of zinc chloride were added 10 g. of chondrosamine hydrochloride, which went rapidly into solution with the development of considerable heat. The reaction mixture was poured into about 200 cc. of water and the acid nearly neutralized with sodium bicarbonate. From this solution crystals of a compound separated out which proved to be a pentacetyl derivative of chondrosamine. It was recrystallized from alcohol until its specific rotation became constant. The yield of the pure substance was about equal to the weight of the hydrochloride used.

The pure compound did not melt, but commenced to turn brown at  $220^\circ$  and was completely decomposed at  $235^\circ$ . It was insoluble in cold water, alcohol and ether, and only slightly soluble in chloroform and acetone. In chloroform solution 0.2500 g. per 50 cc. of the solution gave a reading to the right  $+0.21^\circ$  in a four decimeter tube with sodium light, hence  $[\alpha]_{20}^D = +10.5^\circ$ . After another recrystallization a duplicate measurement gave  $[\alpha]_{20}^D = +11.0^\circ$ .

An acetyl determination made by boiling 0.3050 g. of the compound with 20%  $\text{H}_2\text{SO}_4$ , distilling off the acetic acid and titrating with 0.1 N NaOH gave 77.22% acetic acid. A duplicate gave 76.91% acetic acid. The theoretical amount for chondrosamine pentacetate is 77.12%.

0.2481 g. subst. gave 0.4502 g.  $\text{CO}_2$  and 0.1359 g.  $\text{H}_2\text{O}$ , corresponding to 49.48% C and 6.13% H; 1.000 g. of the substance gave 3.25% N by the Kjeldahl method.

Calc. for  $\text{C}_{18}\text{H}_{28}\text{O}_{10}\text{N}$ : 49.33% C, 5.96% H, and 3.61% N.

<sup>1</sup> *J. Biol. Chem.*, 18, 126 (1914).

**Transformation of  $\alpha$ -Chondrosamine Pentacetate to the Isomeric Beta Form.**—When the  $\beta$ -chondrosamine pentacetate was dissolved in acetic anhydride containing a small amount of  $\text{ZnCl}_2$ , the rotation was found to change upwards from an initial specific rotation of about  $12^\circ$  to a final value of about  $65^\circ$ . After the rotation had reached a constant value the solution was poured into water and the acid nearly neutralized with sodium bicarbonate. A quantity of the original pentacetate separated out at this point. On extracting the mother liquor with chloroform and evaporating the chloroform extract, crystals of a substance were obtained which proved to be the isomeric alpha chondrosamine pentacetate. The following has proved to be a convenient method for the preparation of this compound. Twelve grams of  $\alpha$ -chondrosamine pentacetate were dissolved at the temperature of the steam bath in 100 cc. of acetic anhydride containing about two grams of  $\text{ZnCl}_2$ . The heating was continued until no further change in the rotation was noticed. The solution was poured into 300 cc. of water and the acid nearly neutralized with sodium bicarbonate. The solution was cooled in ice and the crystals of the original substance which here separated out were filtered off. The filtrate was extracted with chloroform and the chloroform extract evaporated to a small volume. On stirring in absolute ether, crystals of the new compound mixed with a small amount of the  $\alpha$ -form separated out. The  $\beta$ -pentacetate was freed from the  $\alpha$ -isomer by dissolving the mixture of crystals in a small amount of absolute alcohol and adding five times this volume of absolute ether. The  $\alpha$ -pentacetate immediately crystallized out and was filtered off. The  $\beta$ -pentacetate was crystallized by evaporating the filtrate in a current of air with the addition from time to time of small quantities of absolute ether. The substance was recrystallized by the above method until its specific rotation became constant and then once more by adding absolute ether to its solution in chloroform. The melting point of the pure substance was  $182\text{--}183^\circ$  corr. This compound is very soluble in cold water, alcohol, ethyl acetate and chloroform, which is in marked contrast to the extreme insolubility of the  $\alpha$ -isomer. In chloroform solution 0.8053 g. of the compound per 25 cc. of the solution gave a reading to the right,  $+6.58^\circ$  in a two decimeter tube with sodium light, hence  $[\alpha]_{17}^D = +102.1^\circ$ . A duplicate measurement in which 0.5343 g. of the substance was used gave  $[\alpha]_{18}^D = +101.3^\circ$ .

Two acetyl determinations made by boiling 0.3075 g. and 0.4169 g. of the  $\beta$ -pentacetate with 50 cc. of 20%  $\text{H}_2\text{SO}_4$ , distilling off the acetic acid and titrating it against 0.1 N NaOH gave 77.03% and 77.30% acetic acid, which agrees with the theoretical, 77.12%.

0.3390 g. gave 0.6122 g.  $\text{CO}_2$  and 0.1832 g.  $\text{H}_2\text{O}$ , corresponding to 49.25% C and 6.05% H; 1.000 g. gave 3.55% N by the Kjeldahl method.

Calc. for  $\text{C}_{16}\text{H}_{22}\text{O}_{10}\text{N}$ : 49.33% C; 5.96% H; 3.61% N.

WARRINGTON, D. C.

## NEW BOOKS.

**Chemistry in the High School.** By E. P. SCHOCH, Professor of Physical Chemistry in the University of Texas, Bulletin 329 and 375 University of Texas. Price, 50 cents.

The book is divided into three parts: I. Equipment; II. A Course of Lessons and Exercises in General Chemistry; III. 'Teachers' Manual. Part I consists of a general discussion of methods to equip the laboratory with respect both to efficiency and economy. In Part II we find a decided departure from the usual arrangement in texts on general chemistry. By omitting all descriptive chemistry the author has brought out in a very clear manner sequence in the development of the subject, leading from the simplest kind of chemical reaction gradually to the more difficult. In the treatment of each kind of reaction, exercises and experiments are given in considerable number illustrating that particular class to the exclusion of all others, as nearly as possible.

The subject is developed in general from the physical chemical standpoint. In the chapter on acids, bases and salts, much time is devoted to conductance experiments illustrating percentage of ionization and metathetical reactions with the idea of showing why the latter take place. In the treatment of oxidation-reduction reactions free use is made of the principles of the electric cell and several experiments are given to show the relation between chemical action in the cell and the general oxidation-reduction reaction. Practically no space, however, is devoted to the illustration of the fundamental laws.

The book gives many references to commercial applications, illustrating the processes used by well-selected experiments. A good descriptive text, as the author states, would have to be used in connection with it. In order to enable the teacher to better correlate the two, Part III is appended which gives many suggestions and ideas that will undoubtedly be of a good deal of help, especially to the inexperienced teacher.

GEO. W. SEARS.

**"Changes in the Food Supply and Their Relation to Nutrition."** By LAFAYETTE B. MENDEL. Yale University Press: New Haven, 1916. 61 pp. Price, 50 cents.

This essay, written for the Second Pan American Scientific Congress at Washington, December, 1915, discusses the production, conservation, preservation, transportation, canning, and refrigeration of food; the deficiency diseases, food requirements, one-sided dietaries, the chemistry of the proteins, the use of oils, customs in diet, and the effect of industrial and social changes as well as other economic and hygienic factors upon the nutrition of nations. These topics are woven together by the author into an exceedingly interesting and stimulating presentation of modern thought on the problems of nutrition and of food economics. The re-

sults of modern research in physiological science are brought to bear upon the problem of the world's food supply, and it is shown that it is idle to make such prophecies as that of Sir William Crookes that the world's wheat supply will soon prove inadequate for the maintenance of the world's inhabitants. It would be hard for both scientists and laymen to find a more illuminating presentation in so small a compass.

CARL L. ALSBERG.

THE JOURNAL  
OF THE  
American Chemical Society

with which has been incorporated the

American Chemical Journal  
(Founded by Ira Remsen)

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[CONTRIBUTION FROM THE DIVISION OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF MINNESOTA.]

THE DISSOCIATION TENSIONS OF CERTAIN HYDRATED  
CHLORIDES AND THE VAPOR PRESSURES OF  
THEIR SATURATED SOLUTIONS.<sup>1</sup>

BY I. H. DERBY AND VICTOR YNGVE.

Received May 13, 1916.

A knowledge of the vapor-pressure relationships of certain hydrated chlorides was required in connection with a problem which is being studied in this laboratory. Since the required data could not be found in the literature, the measurements which follow were made to supply this deficiency. Partington<sup>2</sup> and Foote and Scholes<sup>3</sup> have classified and critically discussed the methods which have been employed for the measurement of the vapor pressures of hydrates. None of the methods they mention seem to combine accuracy, simplicity and ease of manipulation as well as the static method of Smith and Menzies.<sup>4</sup> Since this method is described at length in the exhaustive study cited, only essential details of the apparatus and the precautions taken to secure data of the desired degree of accuracy 0.1 to 2 mm. will be given.

<sup>1</sup> Presented at the meeting of the American Chemical Society, Urbana, Ill., April, 1916.

<sup>2</sup> Partington, *J. Chem. Soc.*, 99, I, 466 (—).

<sup>3</sup> Foote and Scholes, *THIS JOURNAL*, 33, 1309 (1911).

<sup>4</sup> Smith and Menzies, *THIS JOURNAL*, 32, 1412 (1910).

### The Apparatus.

The *isoteniscope* was of the ordinary static type. The confining liquid in all these measurements was a heavy paraffin oil.

Temperature regulation was obtained at the various temperatures below  $75^{\circ}$ , by immersing the *isoteniscope* in a 10 l. cylindrical glass thermostat heated by the method of Derby and Marden.<sup>1</sup>

The especially designed toluene-mercury regulator used allowed of convenient adjustment of temperature of the thermostat at any point within a range of about sixty degrees. At temperatures from above  $50^{\circ}$  up to  $75^{\circ}$  the water in the thermostat was covered with a layer of low melting paraffin. In all cases the regulation was constant within  $0.05^{\circ}$ . For the higher temperatures above  $75^{\circ}$  a benzene-toluene-xylene vapor bath was used. This bath when fitted with a reflux condenser remained constant within  $0.1^{\circ}$ .

The manometer was of the open-end type. The tube of 1 cm. inside diameter was mounted upon a support of thoroughly seasoned wood which bore a paper scale covered with Bakelite varnish. The scale was carefully calibrated by means of a standard cathetometer and during its use showed no variation due to atmospheric changes. After the manometer was permanently placed and adjusted to a truly vertical position, the length of the scale was determined *in situ* by means of a cathetometer. From these observations a scale correction curve was constructed. Scale readings were made by means of a cathetometer to avoid parallax and to give a scale magnification and were estimated to tenths of a millimeter. The barometer, which was read to the nearest tenth of a millimeter, was compared with a standard instrument and the readings were found to be correct. All manometer and barometer readings were corrected to  $0^{\circ}$ . The manometer mercury was purified by dropping it through dilute nitric acid and distilling *in vacuo*.

The *thermometer* used below  $100^{\circ}$  was compared with one recently standardized by the Bureau of Standards and had no scale correction. The thermometer used above  $100^{\circ}$  was corrected at  $100^{\circ}$  by taking the boiling point of water in the usual way. It was then compared with a thermometer certified to  $0.2^{\circ}$  by the Reichsanstalt. In all cases where it was appreciable a correction was made for exposed thread.

**Preliminary Measurements.**—In order to test the accuracy of the method and the applicability of paraffin oil as a confining liquid in the *isoteniscope*, trial measurements of the vapor pressures of water at four temperatures were made. In Table I, under *I*, are given the number of observations made at each temperature, under *t* are given the corrected temperatures, under *p*<sub>1</sub> are given the vapor pressures found, and under *p* are given the values of Scheel and Heuse at the same temperatures taken from the

<sup>1</sup> Derby and Marden, *THIS JOURNAL*, **35**, 1767 (1913).

tables of Landolt-Börnstein. The pressures are given in mm. of mercury.

TABLE I.—VAPOR PRESSURES OF WATER.

I.	<i>t</i> .	<i>p</i> <sub>1</sub> .	<i>p</i> .	Difference.
2.....	25.09	24.0	23.89	+0.1 mm.
2.....	34.15	40.3	40.25	+0.0 mm.
2.....	43.41	66.4	66.22	+0.2 mm.
3.....	54.64	115.8	116.08	—0.3 mm.

It will be seen that the observed values are in good agreement with the true values. Paraffin oil then could safely be employed at least to 55° and above this temperature the errors must be well within a millimeter even at 70–80°. Larger errors due to the vapor pressure of the oil above this temperature would not obscure the relative relationships although leaving the true values somewhat in doubt.

### The Vapor-pressure Relationships of Magnesium Chloride-Water.

The following  $\text{MgCl}_2\text{-H}_2\text{O}$  systems were studied: Saturated solution of  $\text{MgCl}_2\cdot 6\text{H}_2\text{O}$ , saturated solution of  $\text{MgCl}_2\cdot 4\text{H}_2\text{O}$ , and the system  $\text{MgCl}_2\cdot 6\text{H}_2\text{O-MgCl}_2\cdot 4\text{H}_2\text{O}$ . Pure magnesium chloride was recrystallized once from distilled water, washed and dried in a centrifuge fitted with a porcelain basket. Six determinations of the vapor pressure of the saturated solution of the uncrystallized salt at 23.16° gave a mean value of 6.9 mm., while the value at the same temperature for the vapor pressure of the saturated solution of the recrystallized salt was 6.8 mm. The difference is within the limit of error of the method.

In almost all cases where two systems were being studied over the same range of temperature two isoteniscopes were used simultaneously in parallel and so arranged that, by means of suitable stopcocks, either one or both could be connected with the manometer. In this way, as the transition temperature was approached, the method became a differential one and the transition temperature could be determined as exactly as by means of the more cumbersome Frowein tensimeter.

In all these measurements, as well as those which follow, care was taken to bubble vapor out of the bulb in order to secure complete removal of air and, in the case of solutions, to insure saturation. Since the isoteniscopes were connected to the manometer by means of thick-walled rubber tubing, the apparatus was flexible enough to allow the bulbs to be shaken. This, and the small amounts of material needed, insured saturation in the shortest possible time.

In the tabulations for the various systems studied the following abbreviations are used to designate the phases which enter into the equilibrium: Stl. = saturated solution. V. = vapor.  $6\text{H}_2\text{O}$ ,  $4\text{H}_2\text{O}$ , etc., designates the degree of hydration of the salt in the solid phase. For example,  $6\text{H}_2\text{O-Stl.-V.}$  signifies that the phases in equilibrium are for magnesium chloride and water,  $\text{MgCl}_2\cdot 6\text{H}_2\text{O-saturated solution-vapor.}$

Under the phases is placed the temperature range over which the relationship was studied. The curves are also designated by the phases in equilibrium.

In Table II, under *I*, are given the number of observations at each temperature, under *t* are given the temperatures, under *p* are given the vapor pressures of the saturated magnesium chloride solutions. Below 117.2° the solid phase is  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , while above that temperature the solid phase is  $\text{MgCl}_2 \cdot 4\text{H}_2\text{O}$ . Under *p*<sub>6</sub> are given the dissociation tensions of the system  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ – $\text{MgCl}_2 \cdot 4\text{H}_2\text{O}$ .

TABLE II.—VAPOR PRESSURES OF  $\text{MgCl}_2$ – $\text{H}_2\text{O}$  SYSTEMS.

6 $\text{H}_2\text{O}$ –Stl.–V. 10.14°–117.2°. 4 $\text{H}_2\text{O}$ –Stl.–V. 117.2°–138.3°. 6 $\text{H}_2\text{O}$ –4 $\text{H}_2\text{O}$ –V.				6 $\text{H}_2\text{O}$ –Stl.–V. 10.14°–117.2°. 4 $\text{H}_2\text{O}$ –Stl.–V. 117.2°–138.3°. 6 $\text{H}_2\text{O}$ –4 $\text{H}_2\text{O}$ –V.			
<i>I</i> .	<i>t</i> .	<i>p</i> .	<i>p</i> <sub>6</sub> .	<i>I</i> .	<i>t</i> .	<i>p</i> .	<i>p</i> <sub>6</sub> .
5.....	10.14	3.4	....	1.....	104.7	189.9	98.5
3.....	18.05	5.2	....	1.....	108.2	.....	116.8
3.....	25.53	7.7	....	1.....	109.9	195.3	.....
1.....	31.60	....	1.6	1.....	110.2	198.6	.....
4.....	31.65	11.2	....	1.....	110.9	197.6	.....
2.....	41.92	18.5	....	1.....	112.9	198.3	.....
1.....	42.10	....	2.7	1.....	113.1	197.4	146.1
3.....	44.46	21.4	....	1.....	113.6	196.0	.....
5.....	50.96	29.0	....	1.....	114.9	193.7	.....
3.....	55.19	35.4	....	1.....	115.6	.....	165.4
1.....	58.31	....	7.8	1.....	116.0	191.6	.....
1.....	64.10	....	11.3	2.....	116.6	184.0	.....
5.....	64.99	54.1	....	1.....	117.2	169.1	.....
1.....	68.27	....	13.2	1.....	117.7	170.8	.....
1.....	69.38	....	14.6	1.....	118.0	173.7	.....
1.....	74.27	....	21.3	1.....	119.2	181.5	.....
1.....	76.53	....	21.9	1.....	121.2	193.1	.....
1.....	88.85	124.2	41.5	1.....	122.6	205.0	.....
1.....	96.96	154.1	63.1	2.....	125.5	225.3	.....
2.....	99.23	162.7	....	1.....	128.9	247.9	.....
7.....	99.43	163.6	....	1.....	138.3	307.1	.....

The values in Table II were plotted and smooth curves drawn through them. Pressure values could then be read at any temperature. In Table III, under *t*, are given the temperatures, under *p* are given the vapor pressures of the saturated magnesium chloride solutions as read from the curve and under *p*(vH–S) are given the pressures according to van't Hoff<sup>1</sup> and Speranski.<sup>2</sup> From his one experimental value at 25°, van't Hoff has calculated thermodynamically the values below 25°, while Speranski from this data has calculated the values above that temperature. Under *p*(L) are given the values by Lescoeur.<sup>3</sup> Under *p*<sub>6</sub>

<sup>1</sup> Van't Hoff, *et al.*, *Z. physik. Chem.*, **45**, 288 (1903).

<sup>2</sup> Speranski, *Ibid.*, **70**, 319 (1910).

<sup>3</sup> Lescoeur, *Ann. chim. phys.*, [7] **2**, 85.



are given the pressure values for the system  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O} - \text{MgCl}_2 \cdot 4\text{H}_2\text{O}$  as read from the curve.

TABLE III.—VAPOR PRESSURES OF  $\text{MgCl}_2 - \text{H}_2\text{O}$  SYSTEMS AT ROUNDED TEMPERATURES.

<i>t.</i>	6 $\text{H}_2\text{O} - \text{Stl.}-\text{V.}$ 0.0°–117.2°.	<i>p</i> (vH-S).	<i>p</i> (L).	6 $\text{H}_2\text{O} - 4 \text{H}_2\text{O} - \text{V.}$ 35.0°–117.2°.
	4 $\text{H}_2\text{O} - \text{Stl.}-\text{V.}$ 117.2°–140°.			<i>p</i> h.
0.0	2.0 <sup>1</sup>	1.34	...	...
5.0	2.4 <sup>1</sup>	1.96	...	...
10.0	3.2	2.82	...	...
15.0	4.4	4.00	4.4	...
20.0	5.8	5.6	5.75	...
25.0	7.5	7.70	7.5	...
30.0	10.1	...	...	1.5 <sup>1</sup>
35.0	13.4	...	...	1.9
37.5	15.3	...	18.0	...
40.0	17.3	18.98	...	2.5
45.0	21.8	...	...	3.3
50.0	27.6	...	...	4.5
55.0	35.2	...	...	6.2
60.0	43.8	54.11	...	8.3
64.5	53.0	...	53.0	...
65.0	54.1	...	...	11.3
70.0	65.5	...	...	15.1
75.0	79.0	...	...	20.0
77.5	86.4	...	88.0	...
80.0	93.4	134.57	...	26.2
85.0	109.0	...	...	34.0
90.0	127.0	...	...	43.7
95.0	146.0	...	...	56.5
100.0	166.5	...	159.0	75.0
105.0	190.0	...	...	99.5
107.5	194.9	...	...	...
110.0	197.7	...	...	127.5
112.5	197.7	...	...	...
115.0	194.0	...	...	160.0
116.0	190.5	...	...	...
117.0	175.0	...	...	...
117.2	169.1	...	...	169.1
120.0	186.7	...	...	...
125.0	220.0	...	...	...
130.0	255.0	...	...	...
135.0	287.6	...	...	...
140.0	321.5 <sup>1</sup>	...	...	...

The vapor-pressure curves of the  $\text{MgCl}_2 - \text{H}_2\text{O}$  systems studied are shown in Fig. 1. A T is the vapor-pressure curve of the saturated solutions of the hexahydrate. It will be noted that the curve becomes retroflex near the transition temperature T. This is due to the large increase in solubility of the hydrate near its transition temperature. T C is the vapor-

<sup>1</sup> Extrapolated.

pressure curve of the saturated solutions of the tetrahydrate. D T is the vapor-pressure curve of the system  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O} - \text{MgCl}_2 \cdot 4\text{H}_2\text{O}$ . It intersects the curve A T at T.

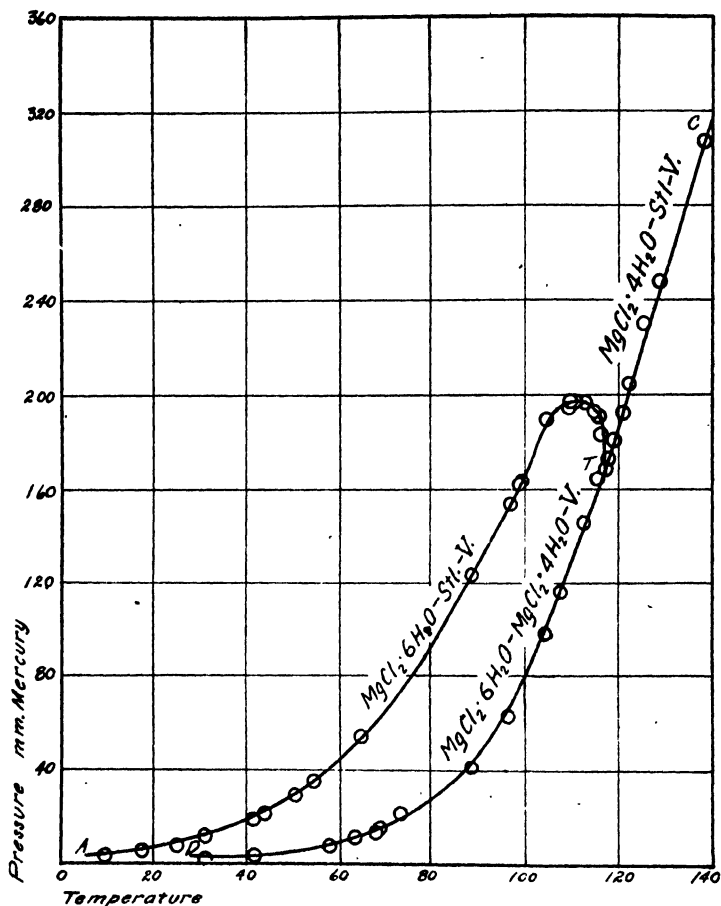


Fig. 1.

### The Vapor-pressure Relationships of Cupric Chloride Water.

Saturated solutions of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  and the system  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O} - \text{CuCl}_2 \cdot \text{H}_2\text{O}$  were studied. The cupric chloride was made from the sulfate by precipitation with sodium carbonate and solution in hydrochloric acid. The twice crystallized salt still showed the presence of small amounts of sulfate. The results should not be affected by this impurity since the sulfate hydrate has a lower vapor pressure than the chloride hydrate.

In Table IV, under I, are given the number of observations at each temperature, under  $t$  are given the temperatures, under  $p$  are given the vapor

pressures of the saturated cupric chloride solutions and under  $p_2$  are given the dissociation tensions of the system  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O} - \text{CuCl}_2 \cdot \text{H}_2\text{O}$ .

TABLE IV.—VAPOR PRESSURES OF  $\text{CuCl}_2 - \text{H}_2\text{O}$  SYSTEMS.

I.	<i>t.</i>	$2 \text{H}_2\text{O} - \text{Sat.} - \text{V.}$ 17.90°–64.45°. <i>p.</i>	$2 \text{H}_2\text{O} - \text{H}_2\text{O} - \text{V.}$ 17.90°–64.18°. <i>p.</i>
I.....	17.90	...	3.7
I.....	26.60	23.3	8.7
2.....	31.40	30.9	11.7
I.....	39.88	49.5	18.8
I.....	53.54	94.3	54.3
I.....	64.18	...	105.6
I.....	64.45	150.6	...

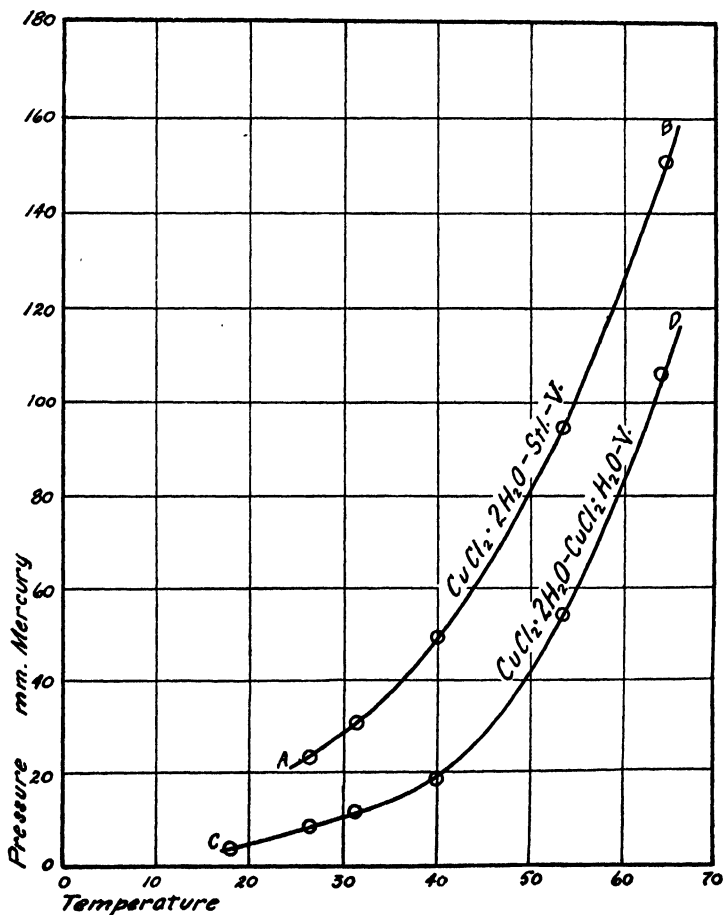


Fig. 2.

The values for every 5°, taken from the curve, are given in Table V.

TABLE V.—VAPOR PRESSURES OF  $\text{CuCl}_2\text{-H}_2\text{O}$  SYSTEMS AT ROUNDED TEMPERATURES.

<i>t</i> .	2 $\text{H}_2\text{O-Sol.}-\text{V.}$ 15.0°-65.0°.	2 $\text{H}_2\text{O-H}_2\text{O}-\text{V.}$ 15.0°-65.0°.	<i>t</i> .	2 $\text{H}_2\text{O-Sol.}-\text{V.}$ 15.0°-65.0°.	2 $\text{H}_2\text{O-H}_2\text{O}-\text{V.}$ 15.0°-65.0°.
	<i>p</i> .	<i>p</i> .		<i>p</i> .	<i>p</i> .
15.0	..	2.6 <sup>1</sup>	45.0	63.5	27.6
20.0	14.7 <sup>1</sup>	5.0	50.0	79.8	41.5
25.0	21.2 <sup>1</sup>	7.8	55.0	100.5	61.2
30.0	28.5	10.7	60.0	125.6	83.5
35.0	37.7	14.1	65.0	154.0 <sup>1</sup>	110.5 <sup>1</sup>
40.0	49.8	19.0			

The vapor-pressure curves of the  $\text{CuCl}_2\text{-H}_2\text{O}$  systems studied are shown in Fig. 2. A B is the vapor-pressure curve of the solution in equilibrium with  $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$ , while C D is the vapor-pressure curve of the system  $\text{CuCl}_2\cdot 2\text{H}_2\text{O-CuCl}_2\cdot \text{H}_2\text{O}$ .

### The Vapor-pressure Relationship of Cobalt Chloride Water.

The following  $\text{CoCl}_2\text{-H}_2\text{O}$  systems were studied: Saturated solutions of  $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ , saturated solutions of  $\text{CoCl}_2\cdot 2\text{H}_2\text{O}$ , and the system  $\text{CoCl}_2\cdot 6\text{H}_2\text{O-CoCl}_2\cdot 2\text{H}_2\text{O}$ . Pure cobalt chloride was recrystallized from distilled water, washed and dried in a centrifuge fitted with a porcelain basket. Careful testing with dimethyl glyoxime failed to reveal any trace of nickel.

In Table VI, under I, are given the number of observations at each temperature, under *t* are given the temperatures, under *p* are given the vapor pressures of the saturated cobalt chloride solutions. Below 52.25° the solid phase was the hexahydrate while above that it was the dihydrate. Under *p*<sub>6</sub> are given the dissociation tensions of the system  $\text{CoCl}_2\cdot 6\text{H}_2\text{O-CoCl}_2\cdot 2\text{H}_2\text{O}$ .

TABLE VI.—VAPOR PRESSURES OF  $\text{CoCl}_2\text{-H}_2\text{O}$  SYSTEMS.

I.	<i>t</i> .	6 $\text{H}_2\text{O-Sol.}-\text{V.}$ 23.4°-52.25°.	6 $\text{H}_2\text{O-2 H}_2\text{O}-\text{V.}$ 23.05°-52.25°.	I.	<i>t</i> .	6 $\text{H}_2\text{O-Sol.}-\text{V.}$ 23.4°-52.25°.	6 $\text{H}_2\text{O-2 H}_2\text{O}-\text{V.}$ 23.05°-52.25°.
		<i>p</i> .	<i>p</i> <sub>6</sub> .			<i>p</i> .	<i>p</i> <sub>6</sub> .
1.....	23.05	..	6.4	1.....	46.84	41.3	33.3
1.....	23.40	13.9	..	1.....	48.60	..	38.4
1.....	24.19	14.7	6.8	1.....	49.23	44.8	39.7
2.....	28.0	..	9.0	1.....	50.02	..	42.0
1.....	28.68	18.4	9.6		51.15	47.2	46.0
1.....	31.9	..	12.1	1.....	51.58	48.0	46.6
1.....	32.65	22.4	12.4	1.....	52.13	..	47.7
1.....	35.98	26.6	16.5	1.....	52.25	48.6	48.6
1.....	39.47	30.5	20.5	1.....	56.44	58.7	..
2.....	39.87	31.1	21.0	1.....	62.12	79.0	..
1.....	39.96	..	21.5	1.....	68.26	105.1	..
1.....	43.92	36.8	27.8	1.....	78.87	170.9	..

The vapor-pressure values at intervals of 5°, taken from the curve, are given in Table VII.

<sup>1</sup> Extrapolated.

TABLE VII.—VAPOR PRESSURES OF  $\text{CoCl}_2\text{--H}_2\text{O}$  SYSTEMS AT ROUNDED TEMPERATURES.

6 $\text{H}_2\text{O--Stl.-V.}$ 20.22°–52.25°. 2 $\text{H}_2\text{O--Stl.-V.}$ 52.25°–80.0°.			6 $\text{H}_2\text{O--Stl.-V.}$ 20.0°–52.25°. 2 $\text{H}_2\text{O--Stl.-V.}$ 52.25°–80.0°.			6 $\text{H}_2\text{O--Stl.-V.}$ 20.0°–52.25°. 2 $\text{H}_2\text{O--Stl.-V.}$ 52.25°–80.0°.			6 $\text{H}_2\text{O--Stl.-V.}$ 20.0°–52.25°. 2 $\text{H}_2\text{O--Stl.-V.}$ 52.25°–80.0°.		
$t$ .	$p$ .		$t$ .	$p$ .		$t$ .	$p$ .		$t$ .	$p$ .	
20.0 <sup>1</sup>	11.8		52.25	48.6		52.25	48.6		52.25	48.6	
25.0	15.3		55.0	54.7		55.0	54.7		55.0	54.7	
30.0	19.7		60.0	60.2		60.0	60.2		60.0	60.2	
35.0	25.1		65.0	91.0		65.0	91.0		65.0	91.0	
40.0	31.3		70.0	114.2		70.0	114.2		70.0	114.2	
45.0	38.7		75.0	144.8		75.0	144.8		75.0	144.8	
50.0	45.9		80.0 <sup>1</sup>	178.5		80.0 <sup>1</sup>	178.5		80.0 <sup>1</sup>	178.5	

The vapor-pressure curves of the  $\text{CoCl}_2\text{--H}_2\text{O}$  systems studied are shown in Fig. 3. The curve A T is the vapor-pressure curve of the solutions in equilibrium with  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ . There is a slight tendency for the curve

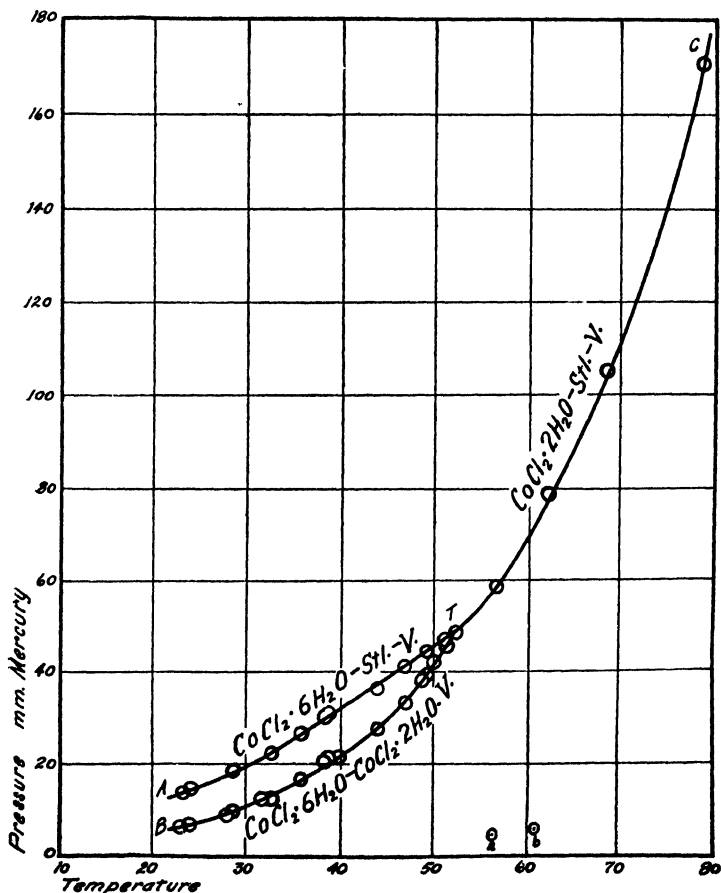


Fig. 3.

<sup>1</sup> Extrapolated.

to flatten out as it approaches the transition point  $T$ . This is due to the increased solubility of the hydrate. The curve  $TC$  is the vapor-pressure curve of the solutions in equilibrium with  $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ . The curve  $BT$  is the vapor-pressure curve of the system  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O} - \text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ . It intersects the curve  $AT$  at  $T$ .

Water vapor was removed from the saturated cobalt chloride solution at a temperature above the transition point until a fall in the vapor pressure indicated the presence of a new phase. At  $56.3^\circ$  the pressure was 4.9 mm., and at  $60.7^\circ$  the pressure was 5.6 mm. (see points  $a$  and  $b$ , Fig. 3). The chloride content of the bulb was then determined by titration with  $0.1\text{ }N$   $\text{AgNO}_3$  using  $\text{K}_2\text{CrO}_4$  as an indicator. The degree of hydration was then calculated and the salt was found to contain 1.82 molecules of water. No evidence of the existence of the tetrahydrate was found.

The vapor-pressure measurements were not refined enough to show any indication of the polymorphic change of the red hexahydrate into the blue hexahydrate which occurs below the transition temperature.

#### The Vapor-pressure Relationship of Nickel Chloride Water.

Vapor-pressure measurements were made on the following  $\text{NiCl}_2 - \text{H}_2\text{O}$  systems: Solutions in equilibrium with  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ; solutions in equi-

TABLE VIII.—VAPOR PRESSURES OF  $\text{NiCl}_2 - \text{H}_2\text{O}$  SYSTEMS.

I.	t.	6 $\text{H}_2\text{O} - \text{Stl.} - \text{V.}$ 19.8°–45.22°.	4 $\text{H}_2\text{O} - \text{Stl.} - \text{V.}$ 36.25°–54.1°	6 $\text{H}_2\text{O} - 4 \text{ H}_2\text{O} - \text{V.}$ 19.8°–36.25°.	4 $\text{H}_2\text{O} - 2 \text{ H}_2\text{O} - \text{V.}$ 25.15°–79.06°.
		p.	p'.	p <sub>h</sub> .	p <sub>h</sub> .
5.....	19.8	9.6	..	7.3	...
1.....	20.6	..	..	7.8	...
2.....	24.1	12.0	..	10.1	...
1.....	24.6	..	..	10.4	...
1.....	25.95	..	..	..	6.0
1.....	26.00	..	..	..	6.1
4.....	30.3	..	..	15.2	...
1.....	30.7	..	..	15.2	...
4.....	31.0	17.5	..	16.1	...
1.....	32.31	..	..	..	8.9
2.....	35.05	21.5	..	20.9	...
2.....	36.25	22.5	22.5	22.5	...
1.....	38.20	..	..	..	14.2
1.....	39.80	26.6	..	..	...
1.....	40.57	..	28.9	..	...
2.....	45.22	33.3	36.7	..	...
1.....	47.69	..	..	..	26.4
1.....	48.34	..	42.6	..	...
1.....	54.1	..	56.4	..	...
1.....	54.50	..	..	..	40.4
1.....	54.63	..	..	..	40.7
3.....	59.63	..	..	..	56.3
2.....	66.34	..	..	..	84.1
1.....	79.06	..	..	..	108.1

librium with  $\text{NiCl}_2 \cdot 4\text{H}_2\text{O}$ ; the system  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ – $\text{NiCl}_2 \cdot 4\text{H}_2\text{O}$ ; and the system  $\text{NiCl}_2 \cdot 4\text{H}_2\text{O}$ – $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$ . The degree of hydration of the last two systems was determined in the manner referred to above for cobalt and they were found to contain 5.74 and 3.78 molecules of water, respectively. The nickel chloride used was "Highest Purity" and was not recrystallized.

In Table VIII, under  $I$ , are given the number of observations at each temperature, under  $t$  are given the temperatures, under  $p$  are given the vapor pressures of the solutions in equilibrium with  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ , under  $p'$  are given the vapor pressures of the solutions in equilibrium with  $\text{NiCl}_2 \cdot 4\text{H}_2\text{O}$ , under  $p_6$  are given the dissociation tensions of the system  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ – $\text{NiCl}_2 \cdot 4\text{H}_2\text{O}$ , and under  $p_4$  are given the dissociation tensions of the system  $\text{NiCl}_2 \cdot 4\text{H}_2\text{O}$ – $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$ .

The vapor-pressure values at every  $5^\circ$ , taken from the curve, are given in Table IX.

TABLE IX.—VAPOR PRESSURES OF  $\text{NiCl}_2$ – $\text{H}_2\text{O}$  SYSTEMS AT ROUNDED TEMPERATURES.

$t$ .	6 $\text{H}_2\text{O}$ –Stl.–V. 15.0°–50.0°. $p$ .	4 $\text{H}_2\text{O}$ –Stl.–V. 36.25°–55.0°. $p'$ .	6 $\text{H}_2\text{O}$ –4 $\text{H}_2\text{O}$ –V. 15.0°–36.25°. $p_6$ .	4 $\text{H}_2\text{O}$ –2 $\text{H}_2\text{O}$ –V. 15.0°–65.0°. $p_4$ .
15.0	8.2 <sup>1</sup>	....	6.5 <sup>1</sup>	4.9 <sup>1</sup>
20.0	9.7	....	7.6	5.2
25.0	12.6	....	10.5	5.9
30.0	16.5	....	14.9	7.6
35.0	21.5	....	20.9	11.0
36.25	22.5	22.5	22.5	....
40.0	26.8	28.1	....	16.3
45.0	33.1	36.3	....	22.7
50.0	39.7 <sup>1</sup>	46.5	....	29.8
55.0	....	58.9	....	39.2
60.0	....	....	....	58.3
65.0	....	....	....	78.3

The vapor-pressure relationships of the  $\text{NiCl}_2$ – $\text{H}_2\text{O}$  systems studied are shown in Fig. 4. The curve A T D is the vapor-pressure curve of the solution in equilibrium with  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ . Here again there is a tendency for the curve to flatten out as it nears the transition point T. We have not noticed any reference in the literature to this increase in solubility of a hydrate near its transition temperature. It would seem to indicate that changes in the physical behavior of a hydrate precede its transformation into a lower hydrate. The curve extends into the unstable region above the transition temperature to D. Here the vapor pressure of the unstable system is lower than that of the stable system. Findley<sup>2</sup> has pointed out that this is due to the greater solubility of the unstable hydrate. The curve B T is the vapor-pressure curve of the system

Extrapolated.

<sup>2</sup> Findley, "The Phase Rule," p. 144.

$\text{NiCl}_2 \cdot 6\text{H}_2\text{O} - \text{NiCl}_2 \cdot 4\text{H}_2\text{O}$ . It cuts the curve A T D at T. The curve T C is the vapor-pressure curve of the solutions in equilibrium with  $\text{NiCl}_2 \cdot 4\text{H}_2\text{O}$ . It is practically a continuation of the curve B T. The curve

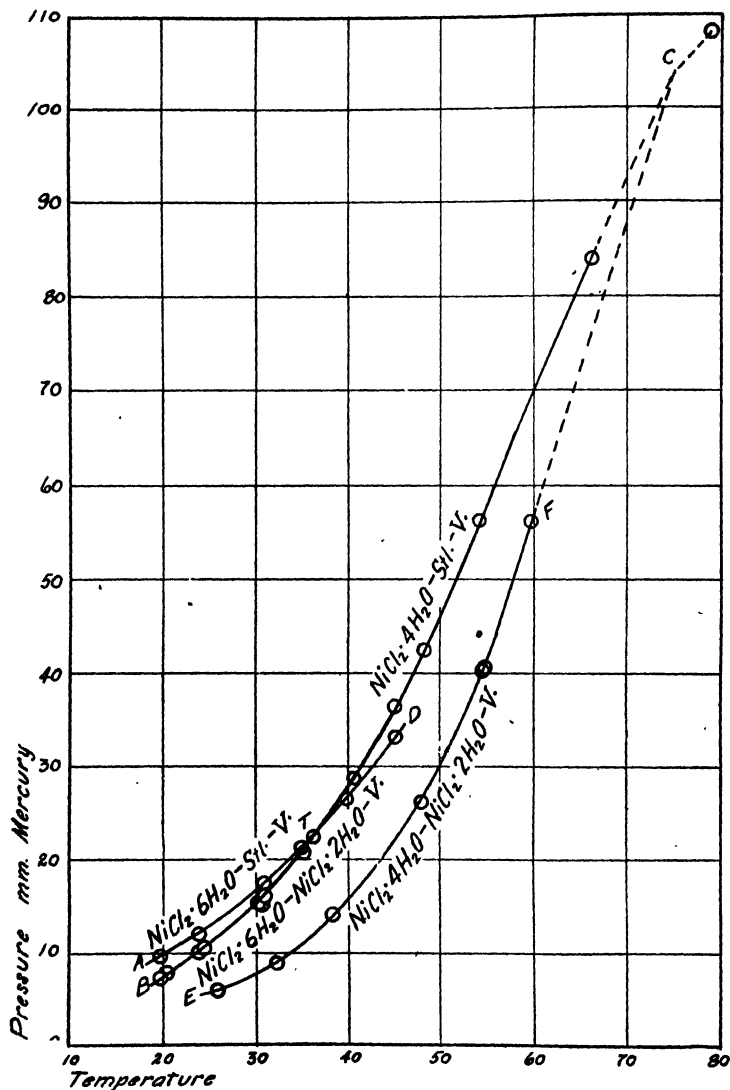


Fig. 4.

E F is the vapor-pressure curve of the system  $\text{NiCl}_2 \cdot 4\text{H}_2\text{O} - \text{NiCl}_2 \cdot 2\text{H}_2\text{O}$ . This should cut the curve T C approximately at  $75^\circ$ ,<sup>1</sup> the transition temperature of the tetrahydrate into the dihydrate. The curves when

<sup>1</sup> Etard, *Ann. chim. phys.*, [7] 2, 545 (1894).



extrapolated, as shown by the dotted lines, intersect at about this point. The transition of the hexahydrate into the tetrahydrate which takes place at  $36.25^\circ$  has never been noted before. Lescoeur<sup>1</sup> found no evidence of the tetrahydrate. The measurements given here seem to point clearly to its existence.

### Summary.

The static method of Smith and Menzies has been employed in determining the dissociation tensions of hydrates and the vapor pressures of their saturated solutions. The method has been found convenient and the data given by it have been consistent and of the required degree of accuracy.

The following systems were studied over the indicated temperature range and transition temperatures were observed as listed:

Systems.	Temp. range.	Transition temp
Components $\text{MgCl}_2\text{-H}_2\text{O}$ .		
$\text{MgCl}_2.6\text{H}_2\text{O-Stl.-V}$ .....	$10.14^\circ\text{-}117.2^\circ$	....
$\text{MgCl}_2.4\text{H}_2\text{O-Stl.-V}$ .....	$117.2^\circ\text{-}138.3^\circ$	....
$\text{MgCl}_2.6\text{H}_2\text{O-MgCl}_2.4\text{H}_2\text{O-V}$ .....	$31.6^\circ\text{-}115.6^\circ$	$117.2^\circ$
Components $\text{CuCl}_2\text{-H}_2\text{O}$ .		
$\text{CuCl}_2.2\text{H}_2\text{O-Stl.-V}$ .....	$26.60^\circ\text{-}64.45^\circ$	....
$\text{CuCl}_2.2\text{H}_2\text{O-CuCl}_2\text{H}_2\text{O-V}$ .....	$17.90^\circ\text{-}64.18^\circ$	....
Components $\text{CoCl}_2\text{-H}_2\text{O}$ .		
$\text{CoCl}_2.6\text{H}_2\text{O-Stl.-V}$ .....	$23.40^\circ\text{-}52.25^\circ$	....
$\text{CoCl}_2.2\text{H}_2\text{O-Stl.-V}$ .....	$52.25^\circ\text{-}78.87^\circ$	....
$\text{CoCl}_2.6\text{H}_2\text{O-CoCl}_2.2\text{H}_2\text{O-V}$ .....	$23.05^\circ\text{-}52.25^\circ$	$52.25^\circ$
Components $\text{NiCl}_2\text{-H}_2\text{O}$ .		
$\text{NiCl}_2.6\text{H}_2\text{O-Stl.-V}$ .....	$19.80^\circ\text{-}36.25^\circ$	....
$\text{NiCl}_2.4\text{H}_2\text{O-Stl.-V}$ .....	$36.25^\circ\text{-}54.10^\circ$	....
$\text{NiCl}_2.6\text{H}_2\text{O-NiCl}_2.4\text{H}_2\text{O-V}$ .....	$19.80^\circ\text{-}36.25^\circ$	$36.25^\circ$
$\text{NiCl}_2.4\text{H}_2\text{O-NiCl}_2.2\text{H}_2\text{O-V}$ .....	$25.95^\circ\text{-}79.06^\circ$	....

The existence of  $\text{NiCl}_2.4\text{H}_2\text{O}$  hitherto in question has been definitely shown.

The tendency of  $p, t$  curves of saturated solutions of hydrated salts to become parallel to the  $t$  axis or even retroflex in close proximity to transition points has been noted in the systems studied. This change must result from a large increase in solubility as this point is reached. This relationship has been treated in detail by Roozeboom<sup>2</sup> from the thermodynamic standpoint.

MINNEAPOLIS, MINN.

<sup>1</sup> Lescoeur, *Ann. chim. phys.*, [6] 19, 547 (1890).

<sup>2</sup> *Z. physik. Chem.*, 4, 31 (1889). Roozeboom's work was kindly called to our attention by the editors.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

## SOLUBILITY.

BY JOEL H. HILDEBRAND.

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CONTENTS.—1. Introduction. 2. Raoult's Law: (a) Kinetic basis; (b) The solubility of gases in liquids; (c) Mutual solubility of liquids; (d) Solubility of solids. 3. Deviations from Raoult's Law: (a) Internal pressure and its effect; (b) Polarity and its effect. 4. Experimental Evidence: (a) Vapor pressure of liquid mixtures; (b) Solubility of gases; (c) Liquids not completely miscible; (d) Solubility of solids; (e) Salt solutions; (f) Metallic solutions. 5. Summary.

## 1. Introduction.

There is scarcely anything more important for a chemist than a knowledge of solubilities, but unfortunately he finds it more difficult to predict how soluble a substance will be in a given solvent than it is to predict almost any other important property. Bodländer,<sup>1</sup> it is true, has made approximate calculations of the solubility in water of some difficultly soluble salts from the electrode potentials of their ions and the heat of formation of the solid salts. Although this is a remarkable step in advance, it is of a very limited applicability, and it suffers, in common with Berthelot's principle of maximal work from the fact that the free energy of a chemical reaction is not equal to the total energy change. Planck<sup>2</sup> has pointed out that the relation between the change in free and total energy in forming a solution, and hence solubilities, could be calculated if we knew, in addition to the heat of solution, the specific heats of solution and pure substances down to absolute zero, the treatment being analogous to the calculation of chemical equilibria by means of the Nernst Heat Theorem. At present our meagre knowledge of specific heats of liquids and solutions makes such a treatment impossible. Furthermore, to be of real use, the calculation of solubility must be made from the properties of the pure substances only, and not from a property of the solution, such as its specific heat, the experimental determination of which may be more difficult than that of solubility itself.

Dolezalek<sup>3</sup> has shown how, assuming Raoult's Law for the vapor pressure of solutions, it is possible to calculate the solubility of gases in liquids. The validity of his calculations will be discussed later.

Washburn and Read<sup>4</sup> have also shown how it is possible to calculate the solubility of solids in liquids in cases where the substances obey Raoult's Law in the liquid state. The significance of this method of calculation is very great, but its scope is limited by the relatively small number of the mixtures which obey Raoult's law throughout the entire

<sup>1</sup> *Z. physik. Chem.*, **27**, 55 (1898).

<sup>2</sup> Planck, "Thermodynamik."

<sup>3</sup> Dolezalek, *Z. physik. Chem.*, **64**, 727 (1908); **71**, 191 (1910).

<sup>4</sup> Washburn and Read, *Proc. Nat. Acad.*, **1**, 191 (1915); *C. A.*, **9**, 1570 (1915).

range of concentration. If the deviations from this law, occurring in most solutions, could be accurately predicted, it would be possible to make accurate calculations of solubilities in general. It has not been possible up to the present time to give an accurate quantitative treatment for these deviations, and the difficulties in the way, it may be added, are very great. It is possible, however, to make certain generalizations of a more qualitative nature, and with their aid very useful predictions of solubility may be made in an approximate way.

## 2. Raoult's Law.

(a) **Kinetic Basis.**—A great deal of the older physical chemistry has had for one of its chief foundation stones the law of van't Hoff for the osmotic pressure of dissolved substances. The fruitful use of this law in dealing with the properties of dilute solutions, and its analogy to the laws for perfect gases, have somewhat blinded chemists to its limitations. Nearly all text-books of physical chemistry still use it to derive the ordinary laws for molecular weight determination, electromotive force of concentration cells, etc., and some investigators still ascribe any variations from these formulas to chemical changes, solvation, etc., forgetting that a large part of the deviation may be due to the inaccuracy of the fundamental equation for osmotic pressure. It has been pointed out by G. N. Lewis<sup>1</sup> and others that Raoult's law is a far better fundamental expression, holding for the simplest solutions throughout the entire range of concentration, when the van't Hoff equation leads to absurd values of osmotic pressure. In spite of the apparent probability of the van't Hoff law due to the analogy between gas pressure and osmotic pressure, it should be noted that Raoult's law has a simpler kinetic basis.

Let us consider a binary liquid mixture composed of  $n_1$  molecules of the component  $X_1$  and of  $n_2$  molecules of the other component,  $X_2$ . Let us denote the vapor pressures of the pure liquids by  $P_1$  and  $P_2$ , respectively, and their partial vapor pressures over the solution by  $p_1$  and  $p_2$ , respectively. If the vapors obey the gas laws, and if the molecules of  $X_1$  and  $X_2$  are sufficiently alike so that they are under the same forces in the mixture as in the pure liquids<sup>2</sup> then it follows, as a mere matter of logic, that since only the fraction  $\frac{n_1}{n_1 + n_2}$  of the molecules of the liquid are of the species  $X_1$ , that the partial pressure of  $X_1$  in the vapor phase,  $p_1$ , is the same fraction of what it would be,  $P_1$ , if all the molecules were of the same species. Hence we write

<sup>1</sup> G. N. Lewis, *THIS JOURNAL*, 30, 668 (1908).

<sup>2</sup> Washburn has defined this limitation by saying that the solution must have "constant thermodynamic environment." *Trans. Amer. Electrochem. Soc.*, 22, 333 (1912).

$$p_1 = P_1 \frac{n_1}{n_1 + n_2}, \text{ and similarly, } p_2 = P_2 \frac{n_2}{n_1 + n_2}. \quad (1)$$

We will consider presently how we may determine whether the molecules of different species are "sufficiently alike" to justify this conclusion, and first indicate, briefly, how the law makes possible the calculation of solubilities of gases and solids in liquids. These calculations have been fully made by the writers referred to, but the repetition seems desirable as an introduction to what is to follow in this paper.

(b) **The Solubility of Gases in Liquids.**—This is expressed in general by the familiar law of Henry, stating that the partial pressure of a gas and its solubility or concentration in a liquid are proportional. Letting  $X_1$  refer to the gas and  $X_2$  to the solvent, we would express this in our notation by the equation

$$p_1 = k \frac{n_1}{n_1 + n_2}.$$

The meaning of the constant  $k$  is made clear by putting  $n_2 = 0$ , when  $k$  becomes equal to the vapor pressure of the pure gas,  $P_1$ . If, as may often be the case, the solution is at a temperature higher than the critical temperature of the gas, then  $P_1$  must be an extrapolated value, as shown at X in Fig. 1. The usual equations giving the actual relation between

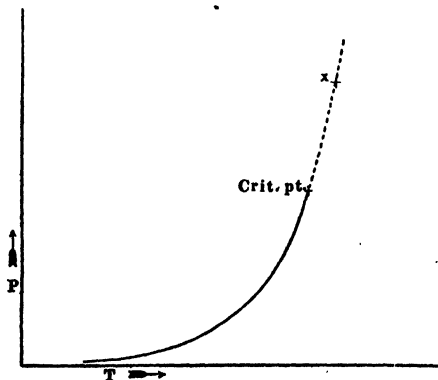


Fig. 1.

vapor pressure and temperature up to the critical temperature must include the effect of the deviation of the vapor from the gas laws as the critical temperature is approached, while Raoult's law, expressed as in this paper, presupposes that the vapor obeys the gas laws. It therefore seems more logical to find  $P_1$  from an equation like the familiar Clausius-Clapeyron equation, than it is to use some one of the empirical equations giving the actual vapor pressures near the critical point. We may say all of this more briefly by stating that  $P_1$  should be considered as the *fugacity* rather than the vapor pressure of the liquid, extrapolated above the critical point.

It should be noted that for the same gas at a given temperature the solubility in all liquids should be the same, according to Raoult's law, when it is expressed in terms of mol-fraction,  $N$ . When, however, it is expressed as the amount of gas in a given weight of solvent, the solvent with the higher molecular weight will dissolve less of the gas *per unit*

*weight*, since there are fewer mols in unit weight of the solvent in this case. Similarly, of two solvents having the same molecular weight, the solubility expressed as amount *per unit volume* of solvent will be greater in the denser solvent, since a unit volume of this solvent would contain more mols.

(c) **The Mutual Solubility of Liquids.**—Whenever liquid mixtures conform to Raoult's law they must be completely miscible, for if there were two liquid phases in equilibrium the partial vapor pressure of each component from each phase would have to be the same, and hence, by Raoult's law, the mol-fractions would be identical, and also the phases.

(d) **Solubility of Solids.**—In considering solutions of solids in liquids we must remember again, letting  $X_1$  denote the species forming the solid phase, that  $P_1$  is the vapor pressure, or better fugacity, of  $X_1$  in the *liquid* form.<sup>1</sup> Since the liquid is the unstable form of  $X_1$  below its melting point, the vapor pressure, or fugacity, of the solid form, which we will call  $P_1'$ , is less than  $P_1$  (see Fig. 2). If, then, solid  $X_1$  is gradually added to liquid

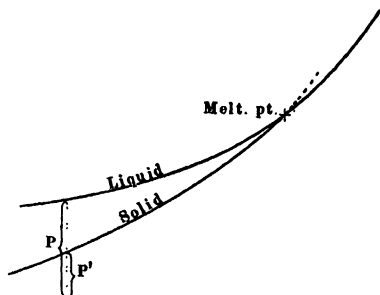


Fig. 2.

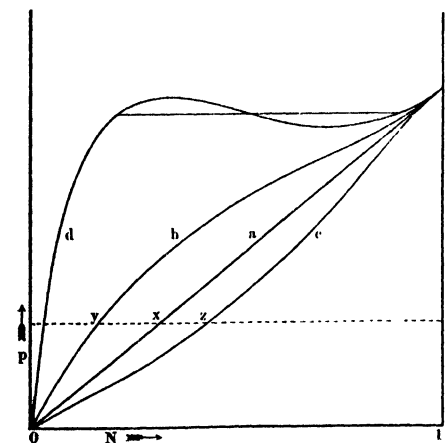


Fig. 3.

$X_2$ , the partial vapor pressure  $p_1$  will increase in proportion to the mol-fraction  $\frac{n_1}{n_1 + n_2}$  (which we will abbreviate into  $N_1$ ) until it becomes equal to  $P_1'$  (at  $x$  in Fig. 3), when no further increase is possible and hence the solution is saturated with respect to the solid, and  $N_1 = P_1'/P_1$ . If, then,  $P_1'/P_1$  can be determined, we can determine the solubility for substances of the class here considered. The ratio  $P_1'/P_1$  is given by the familiar equation<sup>2</sup>

<sup>1</sup> This important limitation has been overlooked by Strachan, *THIS JOURNAL*, 38, 626 (1196). It allows many solutions to remain in the category of ideal solutions that would be needlessly removed from this class by letting  $P_1$  depend on the appearance of a solid phase.

<sup>2</sup> This follows simply by taking the difference between the Clausius-Clapeyron equations for the solid and liquid phases.

$$\log \frac{P'}{P} = \frac{-L_0}{4.58T} + \frac{\Delta\Gamma}{1.99} \log T + I, \quad (2)$$

where  $L_0$  is the molal heat of fusion at absolute zero,  $\Delta\Gamma$  is the difference in the specific heats per mol of the liquid and solid forms, and  $I$  is an integration constant whose value is gotten by putting for  $T$  the melting point on the absolute scale, when  $\log \frac{P'}{P} = 0$ . When  $\Delta\Gamma$  is known  $L_0$  can be found from the molal heat of fusion at a temperature  $T$  by the relation

$$L = L_0 + \Delta\Gamma T. \quad (3)$$

When  $\Delta\Gamma$  is not known we can omit this term without much error, writing Equation 2 simply

$$\log \frac{P'}{P} = \frac{-L}{4.58T} + I. \quad (4)$$

It is obvious that the ratio  $\frac{P'}{P}$ , and hence the solubility of the solid, is smaller the greater the heat of fusion and the higher the melting point of the substance above the temperature chosen.

### 3. Deviations from Raoult's Law.

On investigating the actual vapor-pressure curves for mixtures of normal liquids we find rather good agreement with Raoult's law. Perfect agreement is illustrated graphically by Curve *a* in Fig. 3. With practically all solutions, unless dissociation occurs, the law is obeyed by each component when the other is present in but small amount. Graphically this means that the other types of curves for  $p$ , such as *b*, *c*, and *d*, in Fig. 3, become tangent to the straight line representing Raoult's law when  $N$  approaches unity. In most actual cases, however, as  $N$  becomes smaller, that is, as more of the other substance is added, the partial vapor pressure shows more or less deviation from Raoult's law. The actual pressure is greater than that given by Raoult's law in the majority of instances, as illustrated by *b*, Fig. 3, but is less than that calculated by Raoult's law in some cases, such as *c*, Fig. 3, especially when compounds between the two substances are suspected or known to exist. The percentage deviation generally becomes greater as  $N$  becomes smaller.<sup>1</sup>

These deviations exert a corresponding effect on the solubilities of gaseous or solid substances. Suppose, for example, the behavior is expressed by Curve *b*, Fig. 3, instead of by Curve *a*. This we will call a positive deviation from Raoult's law. It is obvious that saturation with solid  $X_1$  of vapor pressure  $P_1'$  will take place at a smaller value of  $N_1$  (point  $\gamma$ ) than it would be if the Curve *a* were followed (when the solution would

<sup>1</sup> For an exposition of these deviations see Roozeboom, "Heterogene Gleichgewichte" vol. 2 (1904).

be saturated at  $x$ ). Similarly, when a negative deviation from Raoult's law occurs, as shown by Curve  $c$ , more of  $X_1$  can be present in the solution before its partial pressure equals that of the pure solid,  $P_1'$  (at  $z$ ). The same considerations hold when  $X_1$  is a gas, when the partial pressure of the gas,  $p_1$ , takes the place of that of the solid,  $P_1'$ , in the foregoing discussion.

Two kinds of explanation have been offered to account for these deviations from Raoult's law. Dolezalek<sup>1</sup> assumes that any deviation from Raoult's law is caused by some effect which we may call chemical, a change in the number of mols due to the formation of a chemical compound between the two substances or else to a change in the degree of association of one or both constituents. Raoult's law is supposed to hold for each of the species of molecule present in the mixture. The results of this treatment are often quite plausible, and the writer himself has used it in explaining both the vapor pressure and e. m. f. of certain liquid amalgams.<sup>2</sup>

The other basis of explanation is that offered by the van der Waals theory, and has been discussed by van der Waals,<sup>3</sup> van Laar,<sup>4</sup> and Kohnstamm.<sup>5</sup>

Van Laar, for example, points out that we should expect deviations from Raoult's law, even when both liquids are normal, provided their critical pressures are different. He gives a formula involving the heat of mixing, and van der Waals' " $b$ ," and discusses the various types of vapor-pressure curve gotten by altering the constants in the formula.

Kohnstamm also applies the van der Waals theory in a general discussion of curve types.

It seems quite evident that calculations after the method of Dolezalek may be very often without significance. There are many mixtures of liquids, normal according to all ordinary criteria, which give vapor pressures greater than demanded by Raoult's law, one component of which would, according to Dolezalek, have to be considered as associated. Such, for example, are the following pairs: benzene and stannic chloride, bromine and carbon tetrachloride, carbon disulfide and methylal, benzene and hexane, benzene and ether, hexane and aniline. The degree of association that would have to be assumed to account for the observed deviations would entirely remove them from the class of normal liquids. In the case of hexane and aniline,<sup>6</sup> for example, two liquid phases are formed

<sup>1</sup> Dolezalek, *Z. physik. Chem.*, **64**, 727 (1908); **71**, 191 (1910); **83**, 40 (1913).

<sup>2</sup> J. H. Hildebrand, *THIS JOURNAL*, **35**, 501 (1913); *Trans. Am. Electrochem. Soc.*, **22**, 319 (1913); E. D. Eastman and J. H. Hildebrand, *THIS JOURNAL*, **36**, 2020 (1914); **37**, 2452 (1915).

<sup>3</sup> Van der Waals, "Die Kontinuität."

<sup>4</sup> Van Laar, *Z. physik. Chem.*, **72**, 723 (1910); **83**, 599 (1913).

<sup>5</sup> Kohnstamm, *Ibid.*, **75**, 527 (1910).

<sup>6</sup> Unpublished work by Mr. D. B. Keyes of this laboratory.

below  $59.3^\circ$ , which denotes a partial vapor-pressure curve of the type denoted by  $d$  in Fig. 3. It is hard to imagine any kind or degree of association that would give this type of curve and still allow Raoult's law to hold for the various molecular species present. Certain it is that the assumption of the existence of double or triple molecular complexes even to a very great extent never leads to a deviation from Raoult's law sufficient to account for the formation of two liquid phases, as with this particular mixture.

Moreover, it is hard to be consistent in the use of this method when dealing with the same component in different mixtures. Thus, for example, acetone is undoubtedly an associated liquid, and account of this would have to be taken in explaining the vapor pressures when it is mixed with carbon disulfide. However, when dealing with the system acetone-chloroform, Dolezalek neglects such association while calculating the equilibrium involving the compound formed between the two substances.

On the other hand, the van der Waals theory, as applied by van Laar, is inadequate when one of the liquids is associated. Thus methyl alcohol and carbon disulfide, though having nearly equal critical pressures, deviate from Raoult's law to the extent of forming two liquid phases. It should be noted, in fairness, that van Laar recognizes the possibility of uncertainties of this nature.

(a) **Internal Pressure.**—If we seek a clue of a kinetic nature to the deviations from Raoult's law, we find it in the limitation stated earlier while giving the kinetic justification for the law, namely, that the molecules of  $X_1$  and  $X_2$  must be "sufficiently alike so that they are under the same forces in the mixture as in the pure liquids." It has seemed to the writer that the most satisfactory conception to serve as a basis for deciding whether the molecular forces are alike or not would be found in internal pressure. This is the force which, together with the external pressure, opposes the thermal pressure which is due to the kinetic energy of the molecules. In terms of the van der Waals equation

$$p = \frac{a}{v^2} - \frac{RT}{v - b}$$

it is the term  $a/v^2$ , the term  $RT/(v - b)$  being the thermal pressure. It is the cause of the tendency for the number of molecules in the surface of a liquid to be as small as possible, resulting in the phenomena of surface tension. Unfortunately, however, although the conception of internal pressure is a very fundamental one, its definition in experimental terms is very difficult and unsatisfactory. Several methods for calculating internal pressures have been proposed, and values have been published by a number of men. These values vary widely from one another



in the case of the same liquid, as will be seen in Table I. It is not our present purpose to undertake a critique of these calculations, as we are primarily interested in the relative rather than in the absolute values, and the order was found to be substantially the same by the different methods, except for the highly polar liquids, to be discussed later, where two effects are superimposed.

TABLE I.

Liquid.	Internal pressures.					Critical pressure.	Dielectric constant.
	Winther.	Traube.	Walden.	Lewis.	Mathews.		
Octane.....		740	1200	....	1670	25	1.9
Hexane.....		860	1250	....	1700	30	1.9
Pentane.....		....	1210	....	1760	33	...
Ether.....	1220	990	1360	1930	1970	36	4.3+
Xylene.....		....	1650	2820	2400	36	2.3
Stannic chloride.....		1020	1680	....	2500	37	3.2+
Ethyl acetate.....	1490	1140	1730	2640	2460	36	6.1
Toluene.....	1680	1180	1750	....	2650	42	2.3
Methyl acetate.....	1710	1280	....	....	3440	46	7.0
Carbon tetrachloride....	1820	1305	1680	2520	2660	45	2.2
Ethyl chloride.....	1540	1400	1740	....	3000	53	...
Benzene.....	1790	1380	1920	2640	2940	48	2.3+
Chlorobenzene.....		1340	1970	....	....	45	11.0
Chloroform.....	1680	1410	1950	2780	2910	55	5.1
Naphthalene.....		....	1950	....	....	39	...
Chlorine.....		....	2020	....	....	89	1.9
Ethylene chloride.....	2060	1590	2050	....	....	53	10.4
Ethyl iodide.....		....	2060	....	....	..	7.4
Ethylamine.....		....	2060	....	....	66	6.2+
Iodobenzene.....		1420	2140	....	....	45	...
Acetone.....	1790	1390	2200	3190	....	56	22
Pyridine.....		....	2340	....	....	..	12.4
Ethylene bromide.....	2110	1570	2400	....	....	71	4.9
Arsenic Trichloride....		1590	2400	....	....	..	...
Propylalcohol.....	1900	1800	....	....	....	50	22
Carbon disulfide.....	2200	1980	2400	2920	3950	73	2.6
Ethyl alcohol.....	2030	2160	4000	....	3600	63	26
Nitrobenzene.....		....	2470	....	....	...	35—
Bromoform.....		....	2550	....	....	...	...
Methyl alcohol.....	2420	3440	4100	....	....	79	31
Aniline.....		....	2600	....	....	52	7.3
Bromine.....		4800	3000	....	....	...	3.2
Phenol.....		....	3040	....	....	...	9.7
Ammonia.....		....	3900	....	....	114	16
Iodine.....		....	3900	....	....	...	...
Sulfuric acid.....		....	5300	....	....	...	84
Water.....	4900	37300	10200	....	....	218	80
Mercury.....		....	17300	12700	....	456(?)	...

Table I contains values of the internal pressure in atmospheres accord-

ing to Winther,<sup>1</sup> Traube,<sup>2</sup> Walden,<sup>3</sup> W. C. McC. Lewis,<sup>4</sup> and Mathews.<sup>5</sup> The values by Winther, Traube and Lewis are for  $0^\circ$  as calculated by them. Walden gives values only at the boiling point, and in order to obtain values at the same temperature, so that they would be more suitable for comparison, the original values of Walden were reduced to  $0^\circ$  by assuming, according to the van der Waals' theory, that the variation in internal pressure is inversely proportional to  $v^2$ . Considering the uncertainty of the whole calculation, this part of it is relatively unobjectionable. Mathews gives in his paper values for the van der Waals " $a$ ." These were calculated to internal pressures at  $0^\circ$  by dividing by the square of the molecular volumes at that temperature. In the same table are given values for the critical pressures, selected from those given in Landolt-Börnstein. It is not surprising that the order for critical pressures, should be substantially the same, in most cases, as that for internal pressure, since in terms of the van der Waals theory critical pressure is given by  $\frac{8a}{27b^2}$ , while internal pressure is  $\frac{a}{v^2}$ , and  $b$  and  $v$  are closely related. It is well known, however, that the van der Waals equation, using the  $a$  and  $b$  calculated from critical data, does not satisfactorily represent the behavior even of non-associated liquids at much lower temperatures, nor is it possible to do so with any pair of fixed values of  $a$  and  $b$ . Moreover, it seems likely that, for normal liquids,  $b$  varies far more than  $a$ .<sup>6</sup> All of this renders it improbable that equality of critical pressures is the best criterion for our purpose, although it may be exceedingly convenient and useful. We might expect it to be of less value when the  $b$ -values (or molecular volumes) of the substances being compared are very different, and accordingly, as we shall frequently see, chlorine, whose  $b$ -value is small and which would take a considerably different position in the series if the latter were arranged according to critical pressures, behaves rather as we should expect it to when the series is arranged according to internal pressures.

We shall endeavor presently to show, according to the evidence at hand, that approximate equality of internal pressures of normal liquids is an adequate criterion for sufficient likeness in molecular environment for Raoult's law to hold. We shall also see that inequality of internal pressure indicates that the partial vapor pressures will be found greater than given by Raoult's law. It might be expected that two species of

<sup>1</sup> Winther, *Z. physik. Chem.*, **60**, 603 (1907).

<sup>2</sup> Traube, *Ibid.*, **68**, 291 (1909).

<sup>3</sup> Walden, *Ibid.*, **66**, 385 (1909).

<sup>4</sup> Lewis, *Phil. Mag.*, [6] **28**, 104 (1914).

<sup>5</sup> Mathews, *J. phys. Chem.*, **17**, 603 (1913).

<sup>6</sup> T. W. Richards, *THIS JOURNAL*, **36**, 617 (1914).

molecules of different size and attractive power would pack less closely in the mixture than in the pure state, and that the volume of the mixture would be greater than additive, resulting in smaller attractions and greater vapor pressures. In fact, some preliminary calculations give some promise of a formal relation between this expansion, the assumed resulting decrease in internal pressure, and the increase in vapor pressure.

It may be mentioned that Walden, in the paper above referred to, gives a number of generalizations concerning the relation of internal pressure to constitution, in the case of organic liquids.

(b) **Polar Nature.**—There is another factor besides internal pressure which is of profound importance for which the van der Waals theory has not been able adequately to account, which has doubtless been the chief disturbing factor in its application to the liquid state, and in fact to a great deal of the work involving the mass law. That is the polarity of the substance. The nature of this polarity has been discussed by Bray and Branch,<sup>1</sup> and more fully by G. N. Lewis.<sup>2</sup> Molecules which are electrically polar will tend to form larger aggregates, or to associate, just as a mass of similar magnets would do. This polarity results in a molecular attraction, and hence an internal pressure and surface tension, which is greater than it would otherwise be. In an electric field such molecules tend to orient themselves according to their polarity, so that the liquid has a considerable dielectric constant. They also tend to form complexes with polar molecules of different species, "addition compounds." There is also a marked tendency for nonpolar or slightly polar substances to become more polar in the presence of polar substances, as shown, for example, by their greater reactivity when dissolved in polar solvents.

In liquids of this sort we should expect not only the *b* but also the *a* of van der Waals to be very abnormal and variable, and we can see more justification, in mixtures involving a polar liquid, for applying the method of Dolezalek, though even here we dare not assume that each molecular species present will obey the mass law and Raoult's law. The insuperable objection to this treatment seems to be raised by the liquids incompletely miscible, where we would have to make the paradoxical assumption previously mentioned that the mol-fractions are the same in two liquid phases of different composition.

If *X* and *Y* denote nonpolar and polar molecules, respectively, we should expect the attraction between *X* and *Y* to be greater than that between *X* and *X*, but less than that between *Y* and *Y*. This would cause a tendency for the *Y* molecules to form aggregates, even to the extent of separating as a separate phase of greater or less purity, and the deviations

<sup>1</sup> Bray and Branch, *THIS JOURNAL*, **35**, 1440 (1913).

<sup>2</sup> G. N. Lewis, *Ibid.*, **38**, 762 (1916).

from Raoult's law would be very great. In fact highly polar liquids nearly always form two-phase liquid systems with nonpolar liquids.

When two polar liquids are mixed we have rather complicated possibilities. If the attractions between  $Y_1$  and  $Y_2$  happened to be the same as those between  $Y_1$  and  $Y_1$  and between  $Y_2$  and  $Y_2$  we might find Raoult's law followed, but in general one species is more electropositive than the other, and the forces between  $Y_1$  and  $Y_2$  are the greatest, resulting in smaller vapor pressures than would otherwise be the case.

The polarity of a liquid is indicated experimentally by a high dielectric constant, an abnormally great entropy of vaporization,<sup>1</sup> deviation from the Eötvös-Ramsay and Shields rule for surface tension, power to give conducting solutions with electrolytic solutes, etc., etc.<sup>2</sup> A concordant figure for the degree of polarity or the "association factor" can hardly be obtained from the various methods, but we can indicate the polarity roughly by means of the dielectric constant. Values of the dielectric constant are, therefore, given in Table I, selected from those given in Landolt-Börnstein. Where other evidence would modify the conclusions based on the value of the dielectric constant a plus or minus sign is added to the figure to indicate the direction of the modification. For example, stannic chloride is a normal liquid, according to the usual criteria, and gives mixtures with benzene not deviating much from Raoult's law. On the other hand, it is evidently capable of becoming polar, as shown by its solubility and dissociation in water, and its chemical reactivity. It may well be that the symmetry of the molecule gives it, for example, slight moment in an electric field, and hence a small dielectric constant, although the charges within the molecule may be separated considerably, so that the proximity of a strongly polar molecule may distort it, rendering it polar. In the recent paper of G. N. Lewis entitled "The Atom and the Molecule" already cited, it is pointed out that the polar character of a substance is affected by its environment, a slightly polar substance, for example, becoming more polar in the presence of a strongly polar substance. There is no reason to believe that the curve he uses to point out the relation between polarity and "polar influence" would be the same for all substances. We may readily imagine that though two liquids may be equally nonpolar in the pure state they might be influenced unequally by the admixture of a highly polar substance. Such substances as stannic chloride, arsenic chloride, phosphorus trichloride, etc., seem to behave as fairly normal liquids in the pure state, and yet to be capable of polarity in the presence of highly polar substances. The distortion of a symmetrical molecule, previously mentioned, may serve to explain such cases.

If fused salts were included in Table I they would mostly come after

<sup>1</sup> Hildebrand, *THIS JOURNAL*, 37, 970 (1915).

<sup>2</sup> See W. E. S. Turner, "Molecular Association," Longmans, Green & Co., 1915.

water. All the evidence we have goes to show that many molten salts are far more polar than are even the dissociating solvents such as water and ammonia. The latter are not much ionized in the pure state, and their polarity must be due to a separation of the charges in the molecule. Fused salts, on the other hand, seem to be very highly ionized in the pure state, the separation of the charged parts being more or less complete into charged ions, as shown by the high conductivity of fused salts. The resulting liquids are highly abnormal, from the standpoint of the usual criteria, so far as they can be applied, although the term associated is hardly adequate to express their condition. The term polar is far more pertinent. The abnormal character and high internal pressure consequent upon this polar condition is evidenced chiefly by the high surface tension and the deviation from the Eötvös-Ramsay and Shields relation, such as are seen in the following values,<sup>1</sup> figures for water being included for comparison:

TABLE II.

	Temp.	Surface tension.	R. and S. constant.	"Assoc. factor."
NaNO <sub>3</sub> <sup>2</sup> .....	339	106	0.445	10.68
KNO <sub>3</sub> <sup>2</sup> .....	338	110	0.503	8.73
AgCl <sup>3</sup> .....	446-580	...	0.959	3.29
PbCl <sub>2</sub> <sup>3</sup> .....	480-600	...	0.903	3.60
BaCl <sub>2</sub> <sup>4</sup> .....	960	180	....	....
H <sub>2</sub> O.....	20	73	1.13	3.56

Although our knowledge of fused salts is very meagre, we may doubtless make approximate predictions of their relative polarity to serve the purpose to be described later. We may assume that the polarity of a liquid salt is conditioned primarily by the electropositive and electronegative character of its constituents. This is indicated by the electrode potentials, and the electrochemical replacement series, where elements are concerned. This electrochemical character usually accords with the position of the element in the periodic table, the elements becoming increasingly electropositive as we go towards the alkali group, and also as we go from top to bottom of the principal groups. (In the subgroups, such as that including zinc, cadmium and mercury, the most electropositive elements may be found at the top.) The reverse is true for the electronegative character. Information is also gained from the relative strengths of acids and bases, the strongest being those showing the greatest tendency to ionize, and hence being most polar. In accordance with this the alkali halides, for example, would be highly polar, those of silver much less so, silver iodide being less polar than silver chloride. A

<sup>1</sup> See also Walden, *Z. Electrochem.*, **14**, 713 (1908).

<sup>2</sup> Bottomley, *J. Chem. Soc.*, **83**, 1421 (1903).

<sup>3</sup> Lorenz and Kaufler, *Ber.*, **41**, 3727 (1908).

<sup>4</sup> Motylewski, *Z. anorg. Chem.*, **38**, 410 (1903).

substance like lead chloride would be moderately polar, while lead acetate would be but slightly polar. The silicates of the heavier metals would be but slightly polar. An increase of polarity would result from increasing the electronegative character of a weak anion by the formation of a poly-anion, for example, a dichromate would be more polar than a chromate.

It seems, further, that atomic volumes have a great deal to do with polarity. Where these are great there would doubtless be more opportunity for the separation of the charges which produce polarity, the molecule being less compact, and we find, as a matter of fact, that the alkali metals, having the highest atomic volumes of all the elements, give highly polar compounds, followed in this respect by the halogens and the alkaline earths. The element having the smallest atomic volume of all, carbon, gives the least polar of all compounds. The "most normal" liquids we possess are the hydrocarbons of the paraffin series. The difference in atomic volumes may be responsible for the greater polarity of elementary iodine than of chlorine, as shown by the fact that its electrical conductivity in the liquid state is greater than that of chlorine,<sup>1</sup> and also by its greater reactivity. This polarity cannot be due to any difference in the two atoms composing the molecule, but rather to the electron being held under less constraint in the molecule, due possibly to the greater atomic volume as compared with chlorine.

The larger number of factors to be considered with polar liquids, and the lack of information as to their fundamental nature, cause our generalizations in the case of solutions of polar substances in each other to be much less accurate, but even here our predictions may have considerable value.

It will be remarked that in many respects the foregoing considerations concerning salts are essentially the same as those put forward by Abegg and Bodländer<sup>2</sup> in their theory of electro-affinity, which they also apply to the question of solubility. However, there are many serious contradictions that may be drawn from their considerations alone, which may be minimized by considering other factors simultaneously, especially the melting point and the heat of fusion. It must constantly be borne in mind that we are basing our discussion of the deviation from Raoult's law of a mixture of two liquids, and that where the solubility of solids is under discussion we must take into account, first, the polarity, internal pressure, etc., of the supercooled liquid, so far as we know them or are able to predict them, and, second, the instability of the supercooled liquid with respect to the solid form under discussion, as expressed by the ratio

<sup>1</sup> Linde, *Wied. An.*, **56**, 563 (1895); Lewis and Wheeler, *Z. physik. Chem.*, **56**, 179 (1906).

<sup>2</sup> *Z. anorg. Chem.*, **20**, 453 (1899).

P'/P, which may be calculated by the aid of Equation 2 or 4. A discussion of examples later will make this plainer.

The molten metals follow the fused salts at the bottom of the table, being represented by mercury. Here we probably have extreme polarity, the metal being highly dissociated into ions and electrons. However, it may still behave as a normal liquid according to some of the criteria. Mercury, for example, though abnormal according to the surface tension relationship,<sup>1</sup> is quite normal from the standpoint of the entropy of vaporization.<sup>2</sup> Certain it is that the internal pressures of the metals are so high as to preclude mixing with the other liquids, except in the case of the alkali metals in liquid ammonia, and in some fused salts.

We have little basis, as yet, for arranging the metals in the order of their internal pressures, but are left to infer the relative magnitudes of internal pressures from the surface tension, compressibility, and from the tenacity of the metal in the solid form. Table III gives a few values of surface tension selected from Landolt-Börnstein; also values of the compressibility, at 20° C., according to T. W. Richards.<sup>3</sup> One may infer that the internal pressures at the same temperature may increase in the order given in the table.

TABLE III.

	K.	Hg.	Pb.	Ag.	Fe.	Pt.
Temperature.....	62°	15°	325°	1000	1500	2000
Surface tension.....	412	436	510	782	1000	1800
Compressibility $\times 10^6$ at 20° .....	31.7	3.95	2.33	1.01	0.60	0.38

Thus, in spite of the high temperature at which it was observed, it will be noted that the surface tension of molten iron is very high compared with that of the softer metals. This, with the small compressibility and high tensile strength of solid iron, undoubtedly indicates a high internal pressure.

To summarize the effect of internal pressure and polarity, we may say that (1) Raoult's law should be obeyed by mixtures of nonpolar liquids having the same internal pressures; (2) nonpolar liquids of different internal pressures will show greater vapor pressures in the mixture than would be expected from Raoult's law; (3) the same holds true for mixtures of polar with nonpolar liquids; (4) mixtures of polar liquids may show either positive or negative deviations from Raoult's law, but in most cases the latter will predominate; (5) these deviations will modify the predictions of solubility for gases, liquids, and solids, based upon Raoult's law alone, the solubilities being greater where negative deviations occur, and *vice versa*.

<sup>1</sup> Cenac, *Ann. chim. phys.*, [8] 28, 298 (1913); see also J. L. R. Morgan, *Ibid.*, [9] 1, 326 (1914).

<sup>2</sup> Hildebrand, *Loc. cit.*

<sup>3</sup> T. W. RICHARDS, *THIS JOURNAL*, 37, 1643 (1915).

#### 4. Experimental Evidence.

(a) **Liquid Mixtures.**—Having laid down our general principles, let us now compare their application with the observed facts. The following pairs of liquids give mixtures which obey Raoult's law exactly or nearly so: benzene and carbon tetrachloride,<sup>1</sup> benzene and chlorobenzene,<sup>2</sup> benzene and chloroform,<sup>2</sup> benzene and ethylene chloride,<sup>1</sup> chlorobenzene and toluene.<sup>2</sup> It will be observed that all of these liquids have nearly the same values of internal pressure. A small positive deviation, as we would expect, is found in the cases of ethyl iodide with ethyl acetate<sup>3</sup> and benzene with stannic chloride.<sup>4</sup> Larger deviations occur with benzene and carbon disulfide,<sup>5,6</sup> carbon disulfide and carbon tetrachloride,<sup>7</sup> benzene and hexane,<sup>8</sup> benzene and ether<sup>9</sup> and carbon disulfide and methylal.<sup>10</sup> Methylal is not given in the table but it is nonpolar, with a dielectric constant of only 2.7, and it must have a very low internal pressure, as Walden gives for acetal an internal pressure of 1000 atmospheres at 103°. The partial pressure of bromine in dilute solution in carbon tetrachloride is over twice the value calculated from Raoult's law.<sup>11</sup>

Chlorine, on the other hand, obeys Raoult's law rather closely in carbon tetrachloride solution. From the measurements of Jakowkin<sup>12</sup> on the solubility of chlorine in carbon tetrachloride we have calculated the following values for the mol-fraction of chlorine,  $N$ , and the ratio of the partial vapor pressure of chlorine to that of liquid chlorine at the same temperature,  $p/P$ .

$N$ .....	0.00086	0.00225	0.00423	0.00718
$p/P$ .....	0.00092	0.00268	0.00410	0.00673

The corresponding values are obviously almost within the limit of experimental error. This case is significant as showing that the internal pressures furnish a more reliable criterion than do critical pressures. In this case, as may be seen from the table, the former are much more nearly alike than the latter. If our table were arranged according to critical pressures chlorine would have a very different place.

(b) **Solubility of Gases.**—As explained previously, the ratio  $p/P$  for

<sup>1</sup> Zawidzski, *Z. physik. Chem.*, **35**, 129 (1900).

<sup>2</sup> Linebarger, *THIS JOURNAL*, **17**, 615, 690 (1895).

<sup>3</sup> Zawidzski, *Loc. cit.*

<sup>4</sup> Schulze and Hock, *Z. physik. Chem.*, **86**, 445 (1914).

<sup>5</sup> Brown, *J. Chem. Soc.*, **35**, 547 (1879).

<sup>6</sup> Carveth, *J. phys. Chem.*, **3**, 193 (1899).

<sup>7</sup> Brown, *J. Chem. Soc.*, **39**, 517 (1881).

<sup>8</sup> Given without reference by Noyes and Sherrill, "General Principles of Chemistry," p. 27 (1914).

<sup>9</sup> Haywood, *THIS JOURNAL*, **21**, 994 (1899).

<sup>10</sup> Zawidzski, *Loc. cit.*

<sup>11</sup> Unpublished measurements by Lewis and Storch of this laboratory.

<sup>12</sup> Jakowkin, *Z. physik. Chem.*, **29**, 613 (1899).



a solution of a gas in a liquid gives its solubility where Raoult's law holds, even though the value of  $P$  for the gas has to be extrapolated above its critical pressure. The deviations from Raoult's law cannot be predicted with as much satisfaction as in the case of most of the solutions heretofore considered, because we have no knowledge of what places the gases should occupy in the table except as critical pressures may be used for the purpose. However, with the same gas, the solubility in various solvents should depend on the order of the internal pressures of the latter, subject, as always, to the further influence of polarity. The extent to which this is true is seen in Table IV. In calculating the figures here given use is made of the measurements of Just<sup>1</sup> on the solubilities of hydrogen, nitrogen, carbon monoxide and carbon dioxide. The values for methane, ethane, and ethylene are calculated from solubility measurements by MacDaniel,<sup>2</sup> and for ammonia in methyl and ethyl alcohol by de Bruyn.<sup>3</sup>

TABLE IV.<sup>4</sup>

Solubilities of Gases in Terms of Mol-Fraction,  $N \times 10^4$ , when  $p = 1$  Atmosphere.  
20° C.

$p/P$ for gas Solvent.	20° C.				25° C.			
	H <sub>2</sub> .	N <sub>2</sub> .	CO.	CO <sub>2</sub> .	CH <sub>4</sub> .	C <sub>2</sub> H <sub>6</sub> .	C <sub>2</sub> H <sub>4</sub> .	NH <sub>3</sub> .
	10	11	11	178	32	240	148	1020
Hexane.....	...	...	...	...	31	171	159	....
Xylene.....	4.0	6.1	8.9	...	26	...	...	....
Ethylacetate.....	3.2	6.8	9.9	...	..	123	...	....
Toluene.....	3.7	5.3	7.7	108	21	...	...	....
Chloroform.....	...	4.3	6.3	123	..	...	...	....
Benzene.....	2.6	4.1	6.1	94	18	...	125	....
Acetone.....	2.1	4.2	6.5	211	..	...	75	....
Ethylalcohol.....	2.1	3.3	4.5	70	11	55	...	2300
Nitrobenzene.....	1.5	2.6	3.9	112	..	...	...	....
Methylalcohol.....	1.5	2.2	3.0	70	7.4	33	...	2730
Aniline.....	1.16	1.1	1.9	55	..	...	...	....
Carbon disulfide.....	...	1.3	2.0	23	..	...	...	....
Water.....	0.15	0.13	0.19	...	2.4	3.2	8.4	3300

The values of  $p/P$  were gotten by using the data found in Landolt-Börnstein, extrapolating above the critical pressure, where necessary, by the aid of the straight line plot obtained on plotting  $\log p$  against  $1/T$ .  $P$  is the pressure the liquefied gas would have at 20° and 25°, respectively;  $p$  is taken as 1 atmosphere. The solubilities, in terms of mol-fraction, are calculated also for a gas pressure of one atmosphere.

It will be seen that for nitrogen, carbon monoxide, methane, ethane and ethylene, the solubility in the various solvents decreases in essentially

<sup>1</sup> Just, *Z. physik. Chem.*, **37**, 342 (1901).

<sup>2</sup> MacDaniel, *J. phys. Chem.*, **15**, 587 (1911).

<sup>3</sup> de Bruyn, *Rec. trav. chim.*, **11**, 112 (1892).

<sup>4</sup> The writer wishes to express his thanks to Mr. D. B. Keyes for help in the calculations required to prepare this table.

the order given in the table of internal pressures, the gas behaving, in this respect, as would a liquid of low internal pressure. The order for the different gases is not quite identical, but the slight discrepancies are hardly greater than the errors involved. As before, the greatest uncertainty is where the polar solvents are concerned. This is not surprising, as the uncertainties are necessarily greater in such cases on account of our inability to determine how much of the internal pressure is due to the polarity. Carbon dioxide is obviously, from its chemical reactivity, much more polar than the gases previously mentioned, and additional uncertainties are thus introduced, though a distinct increase in solubility in the more polar solvents is evident.

When we come to ammonia, itself highly polar, we find a solubility in polar solvents greater than that indicated by Raoult's law alone.

(c) **Liquids not Completely Miscible.**—Mr. Keyes and the writer have sought a pair of normal liquids that would be incompletely miscible, and have found that aniline, far down in the table, will not mix completely at lower temperatures with the paraffins, standing at the head of the table, though it will mix with all of the normal liquids standing nearer to it. Aniline is slightly polar, which helps to account for this behavior, but it is impossible to account for the deviation from Raoult's law evident in this case by any ordinary assumption as to association according to the method of Dolezalek.

As is well known, the highly polar liquids given in the table do not mix completely with the nonpolar liquids. The internal pressures and the polarity together make relative predictions quite trustworthy. Thus methyl alcohol, more polar than ethyl alcohol, does not mix completely with carbon disulfide whereas ethyl alcohol does. Water, still more polar, is scarcely soluble at all in carbon disulfide. Phenol is more polar than aniline and is accordingly much more soluble in water. Ethyl acetate, though having the same internal pressure as toluene, is much more polar, and hence is far more soluble in water. Other familiar facts are in general accord with the figures in the table.

(d) **Solubility of Solids.**—Iodine, calculated as a supercooled liquid, has the highest internal pressure of any of the normal substances in the table, and accordingly its solutions in most of the liquids represented show large deviations from Raoult's law. To make this evident we must calculate the ratio of vapor pressures for solid and liquid iodine for temperatures in the region of existing solubility measurements. Lewis and Randall<sup>1</sup> give the free energy of liquid iodine at 25° as 460 cal. per gram atom, corresponding to 920 cal. per mol. Since  $920 = -4.58 \times 298 \log P'/P$ , we have  $P'/P = 0.212$ . If Raoult's law held, this figure should represent also the solubility of iodine in terms of its mol-fraction at this tem-

<sup>1</sup> Lewis and Randall, *THIS JOURNAL*, 36, 2259 (1914).

perature. We have calculated the solubility in terms of mol-fraction in bromoform and carbon tetrachloride from measurements by Jakowkin.<sup>1</sup> The solubility in bromoform is given by him only in terms of amount of iodine per liter, so that we have had to make the assumption that the volume of the solution is additive, using for the volume of liquid iodine 59 cc. per mol.<sup>2</sup> The solubilities in carbon disulfide and benzene are gotten from measurements by Arctowski,<sup>3</sup> an extrapolation being necessary in the case of benzene to get the value at 25°. The solubility in chloroform is gotten from data by Hantzsch and Vagt,<sup>4</sup> an interpolation being necessary to reduce to 25°. The following are the resulting values:

	CHBr <sub>3</sub>	CS <sub>2</sub>	C <sub>6</sub> H <sub>6</sub>	CCl <sub>4</sub>	CHCl <sub>3</sub>
P'/P = 0.212; N = 0.066	0.066	0.058	0.047	0.026	0.022

Comparing the order of solubilities with that for internal pressures, we see that the solubility is greatest in bromoform, with the highest internal pressure, and the one nearest to iodine. The value in carbon disulfide comes next, as is to be expected. The internal pressures of the next three liquids are not far apart, and we might expect the solubilities in these liquids to be about the same. This is the case for chloroform and carbon tetrachloride. It is true the order here is reversed, but the moderate uncertainties of the figures for both the internal pressures and solubilities make the small discrepancy of scant significance. The only apparent exception of any magnitude is in the case of benzene, whose internal pressure is very close to those of carbon tetrachloride and chloroform but whose power of dissolving iodine appears to be nearly double what we might expect it to be. This is undoubtedly due to the fact that the solid phase is not pure iodine, but becomes a solid solution of benzene in iodine, as discovered by Beckmann and Stock,<sup>5</sup> allowing more iodine to enter the solution.

Solutions of naphthalene likewise show excellent agreement with the predictions made with the aid of the table. The mol-fraction of naphthalene in saturated solutions in several solvents is given in the following table, in comparison with the value P'/P, calculated from the measurements of Bogojawlenski<sup>6</sup> by means of Equation 2. The heat of fusion per mol is 4440 cal.,  $\Delta T = 5.1$ , the melting point is  $T = 353.1$ .

	CS <sub>2</sub>	CHCl <sub>3</sub>	C <sub>6</sub> H <sub>6</sub> CH <sub>3</sub>	C <sub>6</sub> H <sub>14</sub>	C <sub>2</sub> H <sub>5</sub> OH	P'/P	Temp.
N.....	0.253 <sup>8</sup>	0.303 <sup>7</sup>	.....	0.101 <sup>7</sup>	0.033 <sup>8</sup>	0.286	20°
	.....	.....	0.188 <sup>9</sup>	.....	.....	0.263	16.5°

<sup>1</sup> Jakowkin, *Z. physik. Chem.*, **18**, 585 (1895).

<sup>2</sup> Cf. Dawson, *J. Chem. Soc.*, **97**, 1046 (1910).

<sup>3</sup> Arctowski, *Z. anorg. Chem.*, **6**, 392 (1894); **11**, 272 (1896).

<sup>4</sup> Hantzsch and Vagt, *Z. physik. Chem.*, **38**, 705 (1901).

<sup>5</sup> Beckmann and Stock, *Ibid.*, **17**, 107 (1895).

<sup>6</sup> Bogojawlenski, *Chem. Zentr.*, **76**, II, 945 (1905).

<sup>7</sup> Etard, *Bull. soc. chim.*, [3] **9**, 82 (1893).

<sup>8</sup> Lobry, *Z. physik. Chem.*, **10**, 784 (1892).

<sup>9</sup> Bechi, *Ber.*, **12**, 1978 (1879).

As would be expected from the position of naphthalene in Table I, the values of  $P'/P$  are very close to the values of  $N$  in chloroform, a little less in carbon disulfide with its higher internal pressure, falling off, on the other hand, in toluene and hexane, with their successively lower internal pressures. The polar character of alcohol accounts for the very low solubility in that solvent.

Other data of similar nature is being obtained in this laboratory and will soon be ready for publication, all of which, thus far, is in entire accord with the predictions made.

(e) **Salt Solutions.**—We know so little about the properties of fused salts that we cannot predict relative solubilities in such cases with the certainty that is possible with less polar substances. Several generalizations, however, are possible.

The highly polar character of fused salts, previously referred to, causes all salts, so far as we have been able to determine, to be completely miscible in the liquid state.

The most highly polar salts would be the halides, nitrates, etc., of the alkali and alkaline earth metals, and accordingly these are generally very soluble in polar solvents, showing negative deviations from Raoult's law, in accordance with the principles earlier set forth. This is illustrated in Table V, where the solubility in water at  $25^\circ$  is given in terms

TABLE V.

	Melting point.	Molal heat of fusion.	$P'/P$ calc.	$N$ solubility.
$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ .....	$30^\circ$	8900	0.84	0.44
$\text{H}_3\text{BO}_3$ .....	185	.....	.....	0.016
$\text{AgNO}_3$ .....	218	2580	0.17	0.19
$\text{HgI}_2$ .....	250	4440	0.04	$2 \cdot 10^{-6}$
$\text{NaNO}_3$ .....	333	3690	0.03	0.18
$\text{K}_2\text{Cr}_2\text{O}_7$ .....	397	2980	0.06	0.018
$\text{AgCl}$ .....	455	3050	0.05	$2 \cdot 10^{-7}$
$\text{KCl}$ .....	772	6410	0.0004	0.08
$\text{BaCO}_3$ .....	795	.....	.....	$2 \cdot 10^{-6}$
$\text{Ag}_2\text{S}$ .....	830	.....	.....	$2 \cdot 10^{-7}$
$\text{PbSO}_4$ .....	1100	.....	.....	$3 \cdot 10^{-6}$
$\text{CaF}_2$ .....	1400	.....	.....	$4 \cdot 10^{-6}$
$\text{CaSiO}_3$ .....	1510	.....	.....	0+
$\text{BaSO}_4$ .....	1580	.....	.....	$2 \cdot 10^{-7}$
$\text{Al}_2\text{O}_3$ .....	2020	.....	.....	0+

of mol-fraction, along with values of the melting point, and, where the heat of fusion is known,<sup>1</sup> values of  $P'/P$ , which would equal the solubilities if Raoult's law held. Calcium fluoride and barium sulfate we might

<sup>1</sup> Taken from the data given by Goodwin and Kalmus, *Phys. Rev.*, **28**, 1 (1909), see also Goodwin, *Trans. Am. Electrochem. Soc.*, **21**, 113 (1912) with the exception of the value for  $\text{KCl}$  by Plato, *Z. physik. Chem.*, **55**, 737 (1906), and that for  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ , by Person, *Ann. chim. phys.*, [3] **27**, 250 (1847).

expect to be highly polar in the liquid state. Their insolubility, in spite of polarity, is due to their high melting points, corresponding to a very small value of  $P'/P$ . If the heat of fusion were known, so that  $P'/P$  could be calculated, we would doubtless find that it is less than  $N$  in both cases, so that here, just as with potassium chloride and sodium nitrate, the deviation from Raoult's law would be negative, in accordance with the general principle. The negative deviation from Raoult's law has practically disappeared when we come to the salt of a much less electropositive metal like silver nitrate, and we find in general that the salts of the nobler and hence less electropositive metals become much less polar and less soluble in polar solvents, even if the melting point is not very high. Boric acid, in spite of its low melting point, has obviously very slight polarity, and is accordingly not very soluble in water. When we consider the sulfides of the heavier metals, and especially the silicates, we encounter both small polarity and high melting points, and consequently they are relatively insoluble. With the slightly polar compounds of lower melting point, however, like the acetates, mercuric iodide, etc., we find solubility in the weakly polar organic solvents, for here, as we should expect, the liquids do not show the strong positive divergence from Raoult's law that we find when a polar and a nonpolar substance are mixed.

It must be frankly stated that the mere guess as to the polarity of a molten salt is not sufficient to explain all of the facts. For example, silver iodide, which we might expect to be weakly polar, is far less soluble in water than it would be if Raoult's law held, but it is at the same time far more soluble in liquid ammonia, which is also very polar, although less so than water. We may make a generalization that cannot be deduced from the simple criteria of polarity that we have announced, though it, too, ought ultimately to be brought into accord with the physical properties of the substances, namely, that the tendency to form hydrates, and hence to give negative deviations from Raoult's law and greater solubility in water solution, is greatest for elements at the top of the Periodic Table, whereas the tendency to unite with ammonia, and hence, presumably, to be more soluble in liquid ammonia, is greatest for elements at the bottom of the table. This is illustrated by the abnormally high solubility of magnesium chloride in water, on the one hand, and by the abnormally high solubility of mercuric iodide and silver iodide in liquid ammonia, on the other hand.

In this connection it should be pointed out that the values of  $P'$  and  $P$  which determine the solubility are those of the actual phase which is in equilibrium with the solution. Thus it is the melting point and the heat of fusion of  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ , not of  $\text{CaCl}_2$ , which determine the solubility of calcium chloride at room temperatures. The same applies, of course,

to all solids with solvate of crystallization. Similar modifications must be made when the solid is a solid solution.

It may be stated, finally, that from our standpoint it probably makes little difference whether the solute and the solvent associate with each other to form a new polar complex, or whether there follows a separation of the parts of the original solute molecules into distinct solvated parts, which is electrolytic dissociation. The effect in either case is to reduce greatly the fugacity of the solute,  $p$ , and hence to give strongly negative deviations from Raoult's law. On the other hand, if electrical conductivity is being investigated, it would make a great deal of difference whether or not such dissociation took place, for only then would the ions be free to migrate. This point of view may serve to explain the difference in the values for the degree of dissociation obtained by thermodynamic and by conductivity methods. It is probably folly to expect them to agree, just as it doubtless is folly to expect the different methods for determining the "association factor" of polar liquids to agree.

(f) **Metallic Solutions.**—Here again, our meagre knowledge of the substances in the liquid state prevents any such comparisons as were made earlier. We have discussed previously the probable relative values of the internal pressures of molten metals.

There are many pairs of metals not completely miscible in the liquid state, corresponding to large positive deviations from Raoult's law. These pairs are in accord with what little basis we have at present for prediction. The following examples may be cited: iron-lead, copper-lead, bismuth-iron, aluminum-sodium, chromium-tin, nickel-thallium.

On the other hand, metals near together in the above respects mix readily; giving solid solutions, in many cases, indicating close approximation to Raoult's law in the liquid phase. Examples are silver-gold, bismuth-copper, cadmium-mercury, nickel-cobalt, iron-manganese.

### 5. Summary.

1. The following conclusions can be drawn when Raoult's law holds for a mixture of two liquids:

(a) The solubility of a vapor or gas in terms of its mol-fraction in the solution is given by  $p/P$ , the ratio of the partial pressure of the gas to its saturation pressure. The latter may have to be gotten by extrapolation above the critical pressure.

(b) The solubility of a solid in terms of mol-fraction is given by the ratio of the vapor pressures of its solid and liquid forms at the temperature in question. This can be calculated from the heat of fusion and the melting point, and will be smallest for solids having a high melting point and a large heat of fusion.

(c) When solubility is expressed as weight of solute in a given weight of solvent, the solubility, other things being equal, will be greatest for

solutes of high molecular weight, and for solvents of low molecular weight. When the solubility is expressed as amount of solute in a given volume of the solvent, it is greatest for solvents having low molecular weight and high density.

(2) Deviations from Raoult's law may be ascribed primarily to inequality of internal pressure and to polarity. These factors, and their approximate prediction, have been discussed at some length for various kinds of liquids.

(a) Nonpolar liquids having approximately equal internal pressures obey Raoult's law, and are subject to the previous generalizations.

(b) A difference in internal pressure, with nonpolar liquids, produces a positive deviation from Raoult's law for both components, decreasing the solubility, whether considered with respect to a gaseous or a solid form of the component in question. Very great differences in internal pressure are necessary for incomplete miscibility of the two components in the liquid form.

(c) A polar and a nonpolar liquid show strong positive deviations from Raoult's law, with accompanying effects on solubilities. Most liquids which are not completely miscible belong to this class.

(d) Two polar liquids may show either positive or negative deviations from Raoult's law, usually positive where there is considerable difference in polarity, and negative when both are highly polar. The effects on solubility correspond to the direction of these deviations.

Numerous examples are given justifying the points of view presented.

BERKELEY, CAL.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE WORCESTER POLYTECHNIC INSTITUTE.]

## AN ADIABATIC CALORIMETER.

BY FARRINGTON DANIELS.

Received May 2, 1916.

The cooling correction, which is essential in ordinary calorimetry, is troublesome and uncertain. The adiabatic calorimeter as devised by Richards eliminates this correction, but since it has not received the general acceptance which, in the opinion of the author, it deserves,<sup>1</sup> an attempt has been made in this laboratory to modify the construction so as to bring it into more popular favor. Electrolytic heating, as used by Derby, has made possible the development of a calorimeter which it is hoped will accomplish this purpose.

In common calorimetric practice the temperature is read at frequent intervals and the correction for radiation is calculated by one of several

<sup>1</sup> See criticisms of Dickinson, Bureau of Standards, *Bull.* 11, 206 (1914), and of Jaeger and von Steinwehr, *Z. physik. Chem.*, 54, 428 (1906).

formulae, the best of which is that of Regnault-Pfaunder.<sup>1</sup> Even this is open to objection except for small temperature changes. For commercial work its use entails too much labor, and simpler but less accurate approximations are employed. The simplest method of eliminating radiation is that which employs a vacuum jacketed calorimeter. This is wholly satisfactory in many cases but conduction through the glass may introduce a large and ill-defined heat capacity and if the temperature is not close to that of the room, appreciable exchange of heat with the environment does take place. Furthermore, at high temperatures, condensation of vapor on the cooler cover and upper walls may introduce considerable errors from evaporation.

These difficulties are overcome in the adiabatic calorimeter of Richards, which has been used in the extensive thermo-chemical investigations of high precision at Harvard University.<sup>2</sup> It is so arranged that the temperature of an outer jacket is raised at a rate equal to the rate of rise in the calorimeter. Thus there can be no exchange of heat with the environment. The outer jacket is filled with a strong solution of sodium hydroxide and sulfuric acid is added from a buret as needed, to keep the two temperatures always equal.

The use of strong alkali, however, is objectionable as well as expensive and electrical heating coils may be used instead, as suggested in Richards' first paper. Benedict and Higgins<sup>3</sup> described such a calorimeter in which there was a lag of nearly a minute, necessitating preliminary experiments and giving a determination adiabatic to only about  $0.1^{\circ}$ . Slevenski and Pakovitch<sup>4</sup> have appreciated the advantages of the adiabatic calorimeter. They filled an outer jacket with kerosene and heated it with coils of iron wire of special design. Their results are satisfactory although they are able to keep the process adiabatic to only  $0.1^{\circ}$  or  $0.2^{\circ}$ . In work with Professor Richards, as yet unpublished, the author used a small calorimeter in which a heating coil of nichrome wire was placed in an outer bath of oil. Fifteen seconds were usually required after closing the electrical circuit before the Beckmann thermometer was affected. This time lag was troublesome, but with a slow and regular rise the determination could be kept adiabatic to within  $0.02^{\circ}$  with the help of a rheostat and a previous calibration.

<sup>1</sup> *Pogg. Ann.*, 129, 113 (1866).

<sup>2</sup> *Proc. Am. Acad.*, 41, 3 (1905); 42, 573 (1907); 43, 475 (1908); *THIS JOURNAL*, 31, 1275 (1909); 32, 268, 431, 1176 (1910); 33, 863 (1911); 37, 993 (1915); *Proc. Am. Acad.*, 49, 173 (1913).

<sup>3</sup> *THIS JOURNAL*, 32, 461 (1910).

<sup>4</sup> *J. Russ. Phys. Chem. Soc.*, 46, 1284 (1914). These authors have criticized the descriptions of Richards' calorimeter as being inadequate but the details concerning stirring and adiabatic control for which they searched may be found in the works already cited (*THIS JOURNAL*, 32, 447-450 (1910)), for example.



For rapid or irregular rises electric heating with coils is wholly inadequate and it becomes necessary to eliminate the time lag. Dr. Derby has shown how this can be done in electrolytically heated thermostats<sup>1</sup> and the application to adiabatic calorimeters is obvious. By making the whole water jacket itself the conductor, its temperature rises instantly and uniformly throughout with the passage of the current. In this way it is not necessary to wait for a resistance wire to heat up before the temperature of the bath rises, and rapid stirring becomes unimportant for the heat is not localized.

The construction of a calorimeter along these lines is a simple matter. The one which is shown in Fig. 1 has been in successful operation in this laboratory for over a year, and because it embraces some new features, a brief description is offered. The inner can, A, of thin copper, is filled with water (about half a liter). It contains the source of heat, B, which may be, for example, a combustion bomb or an electric heating coil. It is set into a slightly larger vessel, C, and supported on short pieces of very fine glass tubing so that there is everywhere an air gap of half a centimeter between the walls. Three of these glass supports are soldered to the bottom and six to the sides.<sup>2</sup> A brass collar, D, is soldered to the vessel C, and it is tapered so that a brass cover, E, sets down into it snugly as a ground-glass stopper fits into its bottle. This ring and cover are easily turned out by any machinist in a few hours and ground with emery to give a water-tight joint. Various types of screw covers and rubber rings were tried, but none approached this in simplicity of operation and absolute protection from leakage. The inner vessel is plated with silver and the outer one with nickel, except at the ground joint. They

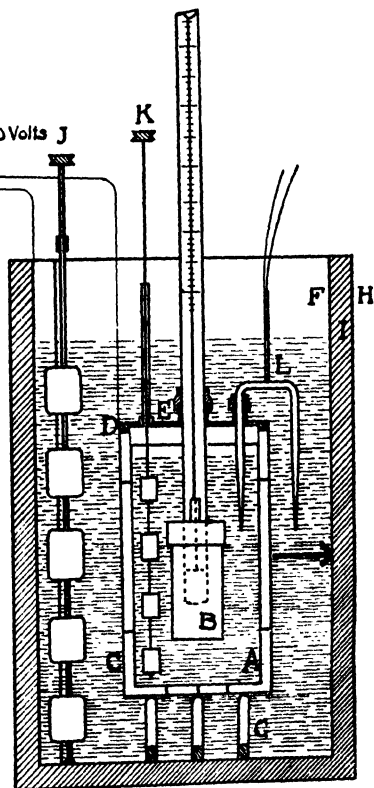


Fig. 1.

<sup>1</sup> THIS JOURNAL, 35, 1767 (1913).

<sup>2</sup> Glass may be soldered to metal readily if it is first roughened with a file or with hydrofluoric acid, platinized and then copper plated.

are supported in a large copper vessel, F, by nine glass tubes G fitting snugly over short brass rods soldered to it. A still larger vessel H, and a packing, I, of insulating material (kieselguhr) diminish the radiation. A stirrer, J, of the propeller type with four blades bent into the form of a screw is driven by a small water motor. A small, semicircular compartment opens from the vessel F, and the stirrer is so placed that half of its revolution is made in the main part of the jacket and half in the compartment.

This arrangement gives a rapid circulation around the sides of the calorimeter and over and under it. The two vessels C and F are connected with the terminals of a 110-volt, alternating current through a knife switch so that the current may be passed directly through the water of the jacket. The stirrer K in the inner can is similar to J, but much smaller. It revolves in a metal sheath which is insulated from the cover by glass tubing. All tubes leading into the calorimeter, whether of glass or of metal, are soldered to the cover and there is, accordingly, no danger from leakage. In order to cut down the space into which the liquid can vaporize, a thin strip of mica is wired around the top of the can, A, and projects above it so as to touch the cover. With this arrangement, liquid can not evaporate to fill the air space at the sides and bottom, but only at the top.

In most adiabatic calorimetry two thermometers have been used; one in the calorimeter and one in the jacket. Rapid readings entail a considerable strain on the observer, so a thermocouple, L, is substituted for them, thereby simplifying the manipulation and increasing the accuracy.<sup>1</sup> The filament of an ordinary tungsten light or a Nernst lamp is focused through a reading lens to a galvanometer and thence to a ground-glass scale or a white paper scale in a dark box. The thermocouple consists of eight copper-constantan junctions packed in paraffin and enclosed in a tapering sheath of very thin glass.<sup>2</sup> The galvanometer (type P as manufactured by Leeds and Northrup) is placed about five meters from the scale and calorimeter. A difference in temperature of  $0.01^{\circ}$  between the inner can and the jacket gives then a deflection of about 1 cm. which may be read without difficulty at a considerable distance.

When the outer jacket is too cold the switch is closed, the alternating current passes through the water of the jacket and the temperature rises instantly. When the thermocouple registers zero the switch is opened and the heating ceases almost at once. With a slow rise of  $0.2^{\circ}$  per minute, or less, it is easy to keep the temperature of the jacket always within  $0.01^{\circ}$  of the temperature of the calorimeter. With a rapid rise of  $1^{\circ}$  per minute the process may be kept adiabatic to within 0.02 or 0.03.

<sup>1</sup> Dickinson has used a thermocouple in an adiabatic calorimeter, Bureau of Standards, *Bull.* 11, 242 (1914).

<sup>2</sup> See White, *THIS JOURNAL*, 36, 2300 (1914) and Adams, *Ibid.*, 37, 484 (1915).

The following test was made, in which the inner liquid was heated intermittently with an electric heating coil so as to obtain an irregular rise. A boy of high school age, after fifteen minutes' practice, watched the thermocouple scale and controlled the switch, while a second observer recorded the temperature of the calorimeter as registered on a thermometer, and the difference between it and the temperature of the jacket as registered by the thermocouple.

Time.		Temperature calorimeter.	Temperature jacket.	Time.		Temperature calorimeter.	Temperature jacket.
Minutes.	Seconds.			Minutes.	Seconds.		
0	0	28.25	-0.01	1	45	30.20	+0.01
0	15	28.60	$\pm 0.00$	2	00	30.50	+0.03
0	30	28.80	-0.02	2	15	30.60	-0.00
0	15	28.90	$\pm 0.00$	2	30	30.80	-0.05
1	00	29.20	-0.01	2	45	31.20	-0.01
1	15	29.40	-0.03	3	00	31.40	$\pm 0.00$
1	30	29.80	-0.02				

The limits of error allowable in the adiabatic control were determined experimentally. It was found that if the temperature of the jacket differed from the temperature of the calorimeter by  $0.1^\circ$  an exchange of heat took place at the rate of 0.5 calorie per minute. If the difference was  $0.01^\circ$ , the heat transfer was 0.05 calorie per minute. This value is of the same order as that found by Richards and Burgess and by Slevenski and Pakovitch in adiabatic calorimeters of larger dimensions. If there is a continuous error of  $0.01^\circ$  in the adiabatic regulation of a calorimeter holding 1 liter an error of 0.01% would be introduced in a determination lasting ten minutes where there was a rise of  $5^\circ$ . Since large errors in the adiabatic control exist but momentarily and since positive and negative differences tend to cancel each other it is safe to say that in the calorimeter described above the AVERAGE difference between jacket and calorimeter may be kept less than  $0.01^\circ$ . This difference could be made smaller by using a more sensitive galvanometer or by increasing the number of junctions in the thermocouple.

With the beam of light from the thermocouple circuit swinging back and forth, the next advance was the automatic control of the heating circuit by means of a selenium cell.<sup>1</sup> The general plan is shown in Fig. 2. When the jacket and the calorimeter are at the same temperature the thermocouple gives a zero reading, and the light rests on the selenium cell, thereby lowering the resistance and closing the relay which breaks the 110-volt heating current. When the calorimeter heats up a little the beam of light moves off from the selenium cell, the relay opens and the heating circuit is closed. The selenium cell is readily made<sup>2</sup> in a few

<sup>1</sup> The use of a selenium cell in such a connection had been suggested in conversation by Mr. A. T. Larson of Harvard University.

<sup>2</sup> See *Sci. Amer. Supplement*, Jan. 27 (1912).

hours from a strip of mica which is notched and wound with No. 32 copper wire. Two wires are used, one starting from each end, and they are wound on alternate notches. These wires are not in electrical contact except through the very large surface of selenium which fills the spaces

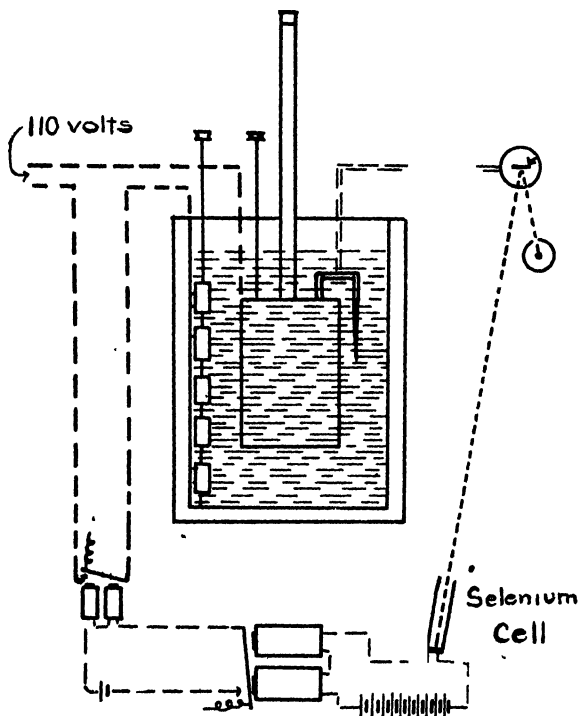


Fig. 2.

used in this circuit is very small and about ten volts from dry cells or small storage batteries are sufficient. A powerful relay of 150 ohms is essential, and to prevent a slight sticking of the contacts, it is vibrated gently by a rod which projects from the stand which holds the pulley wheels. Since the movement of the armature is small, the 110-volt circuit can not be used with it directly, for sparking is too great. Accordingly a second cheap relay is operated by a dry cell through the first relay and it in turn controls the heavy current. Occasionally with a rapid rise the beam of light swings beyond the selenium cell and on to the wrong side, upsetting the whole adiabatic control. To prevent this a stout wire is fastened to the galvanometer box in such a way that the mirror is arrested when the jacket becomes too hot. The tension on the spring of the relay requires frequent adjustment but for a slow rise the determination may be kept adiabatic to within  $0.02^\circ$  or  $0.03^\circ$  without attention.

between them. The selenium powder is spread on the cell, heated to its melting point and molded into place between the wires with a hot glass rod, cooled, and annealed for eight hours at  $215^\circ$  C. A rather large cell (3 cm.  $\times$  20 cm.) and a broad, bright beam of light are desirable. A Nernst lamp with a small convex lens gives an excellent light at a distance of five meters. The selenium cell is placed at the end of a long, black box to cut out the entrance of all light except that from the galvanometer mirror. The current

This synthermal regulator has advantages over that of Richards and Osgood<sup>1</sup> in that it is small and can be attached readily to any calorimeter without inconvenience. The fact that it requires a galvanometer and a good relay is an objection. Because the regulation by hand is such a simple matter, this selenium cell regulator is not recommended for common calorimetric practice unless a large number of determinations are to be made.

It is by no means difficult to alter an ordinary calorimeter so as to make it adiabatic and in fact some of the well-known calorimeters on the market are already surrounded by water jackets. By cutting the two cans apart, inserting glass supports, and attaching a tight cover, one would have an apparatus similar to the one shown in Fig. 1. Hand stirrers could be used to advantage. Even for very rough work it is worth while to eliminate the cooling correction. The water-tight cover may be omitted and a cheap galvanometer is sufficiently sensitive. The stirrer is unnecessary for the temperature in different parts of the jacket does not vary by more than  $0.5^{\circ}$ . Experiments with a crude calorimeter constructed in this way showed a cooling effect of  $0.08^{\circ}$  in ten minutes for a five-degree elevation, whereas under the same conditions without this simple jacket the cooling effect was  $0.37^{\circ}$ . The rate at which the jacket is heated may be very rapid but then the adiabatic control becomes more difficult. If the current is limited to 6 amperes by a fuse plug, 10,000 calories  $\frac{(110 \times 6 \times 60)}{4.18}$  per minute can be introduced, giving a rise of  $5^{\circ}$  per minute with the calorimeter described in Fig. 1. No ordinary calorimetric measurements would require that the jacket be heated up as fast as this. With pure water in the jacket the resistance is high and the heating correspondingly slow but small amounts of electrolyte diminish this resistance greatly. The amperage should be adjusted by the addition of dilute copper sulfate solution so that the rise in the jacket is appreciably more rapid than the most rapid rise in the calorimeter.

Corrosion with an alternating current is not great although the conductivity of the jacket becomes greater and greater, so that the solution must be changed at intervals. If the vessels become seriously corroded they may be renewed by electroplating.

By substituting a high-boiling liquid for water the range of the calorimeter may be extended beyond  $100^{\circ}$ . When a solution of ferric chloride in glycerol fills the jacket the calorimeter may be used up to  $200^{\circ}$ . In case the glycerol is pure it must be heated first as such a solution is a poor conductor at room temperatures. Experiments have shown that the adiabatic control here is just as satisfactory as with the aqueous solutions.

<sup>1</sup> THIS JOURNAL, 37, 1718 (1915).

Professor Derby has suggested (in conversation) the use of fused salts for electrolytically heated thermostats at much higher temperatures, and the same idea could be applied to calorimetry. In fact the use of such a calorimeter should open up a whole new field to accurate physical-chemical measurements.

### Summary.

In conclusion it may be said that adiabatic calorimeters eliminate cooling corrections, thereby excluding errors from precision work and saving time in commercial work. They permit a slow and careful reading of a thermometer while the temperature is constant, and the taking of temperature before and after a determination becomes unnecessary.

Errors from evaporation are negligible in the Richards type of calorimeter or in the modification described in this article, as there is no colder matter in contact with the vapor; and heat can not be lost or gained from the room by conduction. For high temperatures, for slow reactions, or for large temperature differences, these calorimeters are absolutely necessary.

The description of an adiabatic calorimeter of new design is given and it has proved to be accurate and simple of operation.

The automatic control of this calorimeter by means of a selenium cell has been successful, and this very sensitive relay may find application in other work:

The calorimeter herein described is being used in this laboratory in the accurate determination of the specific heats of salt solutions and of organic liquids.

WORCESTER, MASS., April 29, 1916.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY,  
No. 269.]

## THE SPECIFIC CONDUCTIVITY OF PURE WATER IN EQUILIBRIUM WITH ATMOSPHERIC CARBON DIOXIDE.

BY JAMES KENDALL.

Received May 20, 1916.

CONTENTS.—1. Introduction. 2. Previous Work. 3. The Ionization Constant of Carbonic Acid. 4. The Heat of Ionization of Carbonic Acid. 5. The Velocity of the Hydrogen Carbonate Ion. 6. The Carbon Dioxide Content of the Atmosphere. 7. The Solubility of Carbon Dioxide in Water. 8. The Specific Conductivity of the Saturated Solution. 9. Summary.

### 1. Introduction.

The evaluation of the specific conductivity of pure water in equilibrium with the carbon dioxide of the atmosphere is a problem which is of especial importance in connection with the water correction in conductivity determinations.<sup>1</sup>

<sup>1</sup> This subject will be discussed fully in a forthcoming communication.

Carefully prepared conductivity water, when in contact with air, has been found by many observers<sup>1</sup> to possess a constant specific conductivity of  $0.7-0.8 \times 10^{-6}$  reciprocal ohms at the ordinary temperature (usually  $18^\circ$ ). Considering the different methods of preparation employed by different investigators in different laboratories, the numerous values recorded in the literature are remarkably uniform. Whatever method may have been followed and however small the specific conductivity of the water obtained may be when first prepared, its value rises rapidly, on standing, to the limits indicated above, and then remains practically constant.

The suggestion has frequently been made that the conducting impurity in such samples of water consists almost entirely of carbonic acid derived from the atmosphere.<sup>2</sup> It is of interest, therefore, to test whether the *directly-determined* experimental value for the specific conductivity of water in contact with air is in agreement with the value which may be calculated *indirectly* with the help of the following data:

- (a) The ionization constant of carbonic acid.
- (b) The mobility of the hydrogen carbonate ion,  $\text{HCO}_3^-$ .
- (c) The carbon dioxide content of the atmosphere.
- (d) The solubility of carbon dioxide in water.

Concordance between the observed and calculated values will obviously support strongly the validity of the above suggestion.

The figures at present available, however, for such a calculation are only approximate and incomplete. It is the purpose of this paper to establish exact values for all of the quantities tabulated above at  $0^\circ$ ,  $18^\circ$  and  $25^\circ$ , the three temperatures most generally employed in conductivity investigations. It may also be mentioned that an accurate knowledge of these quantities is of some importance apart from the present problem, since their use is essential in many geological studies and in questions of interest in various other fields.<sup>3</sup>

## 2. Previous Work.

The problem has already been taken up, for the temperature of  $18^\circ$ , in the researches of Knox<sup>4</sup> on the conductivity of carbonic acid solutions

<sup>1</sup> A complete list of references will be found in the succeeding article.

<sup>2</sup> See especially Kohlrausch and Holborn, "Leitvermögen der Electrolyte," p. 111 (Leipsic, 1898); Walker and Cormack, *J. Chem. Soc.*, 77, 5 (1900); and Arrhenius, *Meddelanden från K.-Vet. Akads. Nobelinstitut*, Band 2, No. 42 (1914).

<sup>3</sup> For example, see R. C. Wells, *J. Wash. Acad. Sci.*, 5, 617 (1915); Johnston, *THIS JOURNAL*, 38, 947 (1916); Walker and Kay, *J. Soc. Chem. Ind.*, 31, 1013 (1912); Arrhenius, *Phil. Mag.*, 41, 237 (1896).

<sup>4</sup> Knox, *Ann. der Physik.*, 54, 44 (1895). The figures given in this and all succeeding references have (where necessary) been recalculated from Siemens' units to units of the reciprocal ohm.

and of Walker and Cormack<sup>1</sup> on the dissociation constants of very weak acids.

The conductivity measurements of Knox, as will be shown in a later section of this paper, are obviously considerably in error; the method employed by him for the calculation of the solubility of carbon dioxide in water under atmospheric conditions is also inaccurate. Consequently, his conclusion that the calculated value for the specific conductivity of water in equilibrium with the carbon dioxide of the atmosphere ( $0.60 \times 10^{-6}$  reciprocal ohms at  $18^\circ$ ) is substantially identical with the direct experimental value of Kohlrausch and Heydweiller<sup>2</sup> ( $0.64 \times 10^{-6}$  reciprocal ohms at  $18^\circ$ ) is not entirely convincing.

The results obtained by Walker and Cormack are of much greater value. It was found that carefully purified Dundee water (prepared by three successive distillations, namely from alkali, from phosphoric acid, and without the addition of any chemical) possessed a specific conductivity of  $0.75 \times 10^{-6}$  reciprocal ohms at  $18^\circ$ . The ionization constant of carbonic acid at this temperature was found to be  $3.04 \times 10^{-7}$  (a value differing by 20% from that obtained by Knox). The dilution of a solution saturated with carbon dioxide at a pressure of 760 mm. was taken as equal to 24 liters; according to Bunsen's absorption data.<sup>3</sup> Assuming the partial pressure of carbon dioxide in air to be 0.0003 atmosphere,<sup>4</sup> the specific conductivity of water in equilibrium with atmospheric carbon dioxide was calculated to be  $0.70 \times 10^{-6}$  reciprocal ohms at  $18^\circ$ . The agreement of this value with that directly determined is clearly close enough to support the assumption that the specific conductivity of water in contact with air is to be ascribed almost entirely to dissolved carbon dioxide. Further confirmation was found in the results obtained from the application of a correction made under this assumption to the conductivity values of aqueous solutions of phenol.<sup>5</sup> This will be more fully discussed in the following communication.

It must be admitted, however, that the greater part of the data employed by Walker and Cormack in the above calculation is only approximate. In fact, the only exact figure utilized is that for the ionization constant of carbonic acid, and even that differs considerably from the value found by Knox.

In the present paper, therefore, the conductivity measurements of Walker and Cormack for the temperature of  $18^\circ$  have been repeated, and results have also been obtained for two other temperatures— $0^\circ$  and

<sup>1</sup> Walker and Cormack, *J. Chem. Soc.*, 77, 5 (1900).

<sup>2</sup> Kohlrausch and Heydweiller, *Z. physik. Chem.*, 14, 317 (1894).

<sup>3</sup> These results may be in error by several per cent., as may be seen by reference to the original paper, *Ann.*, 93, 1 (1855).

<sup>4</sup> Obviously only a very rough approximation.

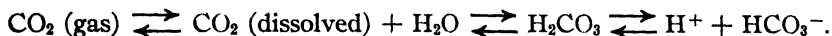
<sup>5</sup> Walker and Cormack, *J. Chem. Soc.*, 77, 18 (1900).



25°. Exact determinations have been made regarding the carbon dioxide content of the atmosphere, and more recent and accurate data for the solubility of carbon dioxide in water have been employed in the final calculations. The different steps necessary for the exact solution of the problem are taken up in order below. The summarized results will be found in Section 8.

### 3. The Ionization Constant of Carbonic Acid.

A solution of carbon dioxide in water possesses considerable electrical conductivity, due to the fact that the gas does not exist in solution merely as carbon dioxide, but also combines with the solvent to give the acid  $\text{H}_2\text{CO}_3$ , which ionizes into  $\text{H}^+$  and  $\text{HCO}_3^-$ . The complete equilibrium to be considered<sup>1</sup> is



(The secondary dissociation of  $\text{HCO}_3^-$  into  $\text{H}^+$  and  $\text{CO}_3^{2-}$  is so minute<sup>2</sup> that it need not be taken into consideration here.)

The conductivity of carbonic acid solutions was first investigated by Pfeiffer<sup>3</sup> at temperatures of 0° and 12.5°. Ionization constants were unknown quantities when these measurements were published, and since the results of Pfeiffer, recalculated according to the dissociation theory, have not previously been tabulated, they are summarized in the following table. The first column indicates the dilution of the solution in liters (V); the second the equivalent conductivity<sup>4</sup> ( $\Lambda$ ); the third the dissociation constant  $k$ , multiplied by  $10^7$  to avoid an excess of zeros. Subsequent tables are arranged according to the same scheme.

TABLE I.—CARBONIC ACID (PFEIFFER).

Temperature, 0°.			Temperature, 12.5°.		
V.	$\Lambda$ .	$k \times 10^7$ .	V.	$\Lambda$ .	$k \times 10^7$ .
2.37	0.167	1.68	2.79	0.304	3.18
3.07	0.188	1.65	3.29	0.334	3.25
3.85	0.213	1.69	5.27	0.421	3.23
4.39	0.235	1.81	6.59	0.450	(2.95)?
13.38	0.458	(2.26)?	13.38	0.661	3.14
$\infty$	264.0	..	$\infty$	323.0	..

Whence  $k = 1.7 \times 10^{-7}$

Whence  $k = 3.2 \times 10^{-7}$

The constancy of the values in the last column is by no means all that could be desired at either temperature, and the dissociation constants given are, at best, only approximate values. This is probably due to the poor quality of water (specific conductivity =  $3.2 \times 10^{-8}$  reciprocal ohms) employed in the investigation; the conducting impurities present

<sup>1</sup> The discussion of this equilibrium is deferred to a later section; see page 1493.

<sup>2</sup> McCoy, *Am. Chem. J.*, 29, 437 (1903); Johnston, *THIS JOURNAL*, 37, 2001 (1915).

<sup>3</sup> Pfeiffer, *Ann. Phys.*, 23, 625 (1884).

<sup>4</sup> The determination of the equivalent conductivity at infinite dilution ( $\Lambda_\infty$ ), which is necessary for the evaluation of  $k$ , is described in a following section.

might suffice to account for a considerable portion of the measured conductivities.

The measurements of Knox<sup>1</sup> may also be used to calculate the ionization constant of carbonic acid at temperatures of 12.5° and 18°. Knox did not attempt to carry out these calculations himself, in an abstract<sup>2</sup> an erroneous value is given, and Walker and Cormack<sup>3</sup> have given one series of results under the old Siemens units. The complete results of Knox have, therefore, been calculated to modern units and are summarized in Table II, below.

TABLE II.—CARBONIC ACID (KNOX).

Temperature, 12.5°.			Temperature, 18°.		
V.	$\Lambda$ .	$k \times 10^7$ .	V.	$\Lambda$ .	$k \times 10^7$ .
10.48	0.603	3.32	12.61	0.778	3.76
12.24	0.652	3.32	14.54	0.838	3.79
15.43	0.735	3.34	24.9	1.090	3.75
20.79	0.853	3.36	53.2	1.581	3.70
29.77	1.019	3.35	125.0	2.445	3.77
$\infty$	323.0	....	$\infty$	354.0	....
Whence $k = 3.34 \times 10^{-7}$			Whence $k = 3.75 \times 10^{-7}$		

The constancy of the values obtained by Knox appears to be quite satisfactory; the dissociation constant at 12.5° is also in good agreement with that given by the measurements of Pfeiffer. Nevertheless the later results of Walker and Cormack indicate that Knox's measurements also are considerably in error. The cause is again, most probably, the poor grade of water (specific conductivity as high as  $2.8 \times 10^{-6}$  reciprocal ohms) used in the determinations. Thus, at dilution 125 in Table II, the conductivity of the water amounted to 12% of the total conductivity of the solution. For dilutions higher than 125,  $k$  is no longer a constant.

The careful measurements of Walker and Cormack at 18° are recalculated to modern units and given in Table III, below. A column indicating the ratio of the ionized to the total solute,  $[\alpha]$ , is added.

TABLE III.—CARBONIC ACID (WALKER AND CORMACK), 18°.

V.	$\Lambda$ .	$\alpha$ .	$k \times 10^7$ .
27.5	1.033	0.00289	3.05
55.0	1.454	0.00407	3.03
82.5	1.784	0.00500	3.04
110.0	2.052	0.00575	3.02
$\infty$	354.0	...	..

Whence  $k = 3.04 \times 10^{-7}$

The value of the ionization constant is about 20% less than the value calculated from Knox's figures, corresponding to an actual difference in the conductivity of 10%. The better quality of the water used (specific

<sup>1</sup> Knox, *Loc. cit.*

<sup>2</sup> *Z. physik. Chem.*, **17**, 186 (1896).

<sup>3</sup> Walker and Cormack, *J. Chem. Soc.*, **77**, 9 (1900).

conductivity =  $0.75 \times 10^{-6}$  reciprocal ohms) and the fact that a more exact method was employed for measuring the concentration of the solutions<sup>1</sup> cause the investigators to conclude that their own numbers are probably the more accurate.

This conclusion is confirmed by the present author's measurements, which are given in Table IV, below. The experimental method adopted for the conductivity determinations was precisely that followed and described in previous investigations.<sup>2</sup> A Cantor cell<sup>3</sup> (with large electrodes only a small distance apart) was employed, this type possessing the advantage that successive dilutions can be made rapidly and accurately *within* the cell. A rotating commutator and a galvanometer were used in place of the more general induction coil and telephone, and gave satisfactory results throughout. The bridge employed was a three-meter platinum wire with one thousand divisions; readings could be obtained and duplicated to one-tenth of a division at all dilutions, the galvanometer being used as a zero instrument. The cells were immersed when in use in a large electrically-controlled thermostat, the greatest variations in temperature during the observation period being  $0.005^{\circ}$ .

The solutions of carbonic acid were prepared by passing pure carbon dioxide (obtained by the action of tartaric acid<sup>4</sup> on sodium carbonate) first through several wash-bottles containing conductivity water, and finally through the water (60 cc. in volume) contained in the Cantor cell. The water employed possessed a specific conductivity of  $0.60 \times 10^{-6}$  reciprocal ohms at  $0^{\circ}$ ,  $0.75 \times 10^{-6}$  reciprocal ohms at  $18^{\circ}$ , and  $0.85 \times 10^{-6}$  reciprocal ohms at  $25^{\circ}$ . The method of its preparation will be described fully in the following paper.

The concentration of carbonic acid in each solution was determined *immediately after* the conductivity measurements had been completed, by running out half of the volume (30 cc.) from the cell and estimating its carbon dioxide content by a suitable modification of the Walker-Pettenkofer method.<sup>5</sup> The results obtained from duplicate experiments were in agreement within 0.2%.

An examination of the last column of Table IV will show that the ionization constants obtained at each temperature are *true* constants

<sup>1</sup> A modification of Pettenkofer's method; see Walker, *J. Chem. Soc.*, 77, 1110 (1900).

<sup>2</sup> Kendall, *J. Chem. Soc.*, 101, 1275 (1912).

<sup>3</sup> Cantor, *Z. Elektrochem.*, 9, 922 (1903).

<sup>4</sup> If the carbon dioxide is prepared by the action of hydrochloric acid on marble in the usual manner, a trace of hydrochloric acid is invariably carried over into the conductivity cell, in spite of the several intervening wash-bulbs.

<sup>5</sup> Walker, *Loc. cit.* The solution was run directly into a bottle containing air free from  $\text{CO}_2$ , excess of baryta solution of known concentration added, and the normal procedure then followed.

throughout the whole range of dilutions. The value obtained at  $0^\circ$  is much higher than that given by the measurements of Pfeiffer; the value at  $18^\circ$  is in good agreement with that of Walker and Cormack.

TABLE IV.—CARBONIC ACID (KENDALL).

V.	$\Lambda$ .	$\alpha$ .	$k \times 10^7$ .
T. $0^\circ$ .			
25.4	0.631	0.00239	2.25
38.3	0.770	0.00292	2.23
50.0	0.888	0.00336	2.27
76.3	1.081	0.00409	2.21
99.8	1.242	0.00471	2.23
152.6	1.548	0.00586	2.27
$\infty$	264.0	...	..
Whence $k = 2.24 \times 10^{-7}$			
T. $18^\circ$ .			
30.9	1.100	0.00311	3.13
42.0	1.281	0.00362	3.12
61.2	1.550	0.00438	3.14
83.4	1.792	0.00506	3.09
$\infty$	354.0	...	..
Whence $k = 3.12 \times 10^{-7}$			
T. $25^\circ$ .			
36.4	1.403	0.00357	3.51
51.3	1.659	0.00422	3.48
72.8	1.977	0.00503	3.49
102.4	2.341	0.00595	3.48
145.5	2.820	0.00717	3.55
$\infty$	393.4	...	..
Whence $k = 3.50 \times 10^{-7}$			

#### 4. The Heat of Ionization of Carbonic Acid.

The accuracy of the values for the ionization constant of carbonic acid given in Tables I–IV may be tested by calculating, from the figures for two different temperatures, the heat of ionization,  $Q$ , according to the van't Hoff formula

$$\log k_1 - \log k_2 = (Q/2.303 R) (1/T_1 - 1/T_2)$$

(where  $k_1$  and  $k_2$  are the dissociation constants at absolute temperatures  $T_1$  and  $T_2$ , respectively) and comparing the calculated value with that obtained by direct thermal measurements. The heat of the reaction:  $\text{H}_2\text{CO}_3(\text{aq.}) = \text{H}^+ + \text{HCO}_3^-$  is the heat of mixture of one mol  $\text{H}_2\text{CO}_3$  and one mol  $\text{NaOH}$ , less the heat of neutralization of one equivalent of a strong acid. From the measurements of Thomsen<sup>1</sup> it is equal to  $-2800$  cal.

The values for  $Q$  as calculated from the results tabulated above are as follows:

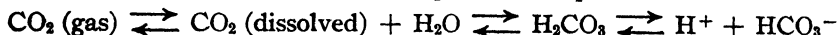
<sup>1</sup> Thomsen, "Thermochemische Untersuchungen," Leipzig (1882).

TABLE V.—HEAT OF IONIZATION OF CARBONIC ACID.

Temperature interval.	Observer.	Heat of ionization.
0°–12.5°	Pfeiffer	—7850 cals.
12.5°–18°	Knox	—3480 cals.
0°–25°	Kendall	—2890 cals.
0°–18°	Kendall	—2910 cals.
18°–25°	Kendall	—2830 cals.

The agreement of the values of the present paper with that directly determined is very satisfactory, the results of Pfeiffer and of Knox, on the other hand, give figures which are far too high.

A careful consideration of the complete equilibrium in carbonic acid solutions, however, introduces a disconcerting factor into the above calculation. The "ionization constants" and "heats of ionization" given in the tables preceding have not the exact signification that is usually attached to those quantities. The equilibrium equation



shows that the nonionized portion of the solute exists partly as  $\text{H}_2\text{CO}_3$  and partly as  $\text{CO}_2$  in the solution. The *true* ionization constant:  $(\text{conc. H}^+)/(\text{conc. HCO}_3^-)/(\text{conc. H}_2\text{CO}_3)$  will therefore be different from (and greater in value than) that calculated in Tables I–IV according to the formula:  $(\text{conc. H}^+)/(\text{conc. HCO}_3^-)/(\text{conc. H}_2\text{CO}_3 + \text{conc. CO}_2)$ . Similarly the *true* heat of ionization will differ from that calculated above, in which the heat of the reaction  $\text{CO}_2(\text{dissolved}) + \text{H}_2\text{O} = \text{H}_2\text{CO}_3$  is also included.

Owing to the fact that the ratio:  $(\text{conc. CO}_2)/(\text{conc. H}_2\text{CO}_3)$  in the solution will not vary with the dilution (providing only dilute solutions are investigated,<sup>1</sup> the "ionization constants" obtained in the above tables still show a constant value, although they are not the *true* ionization constants. The true values could be found from them if the ratio  $(\text{conc. CO}_2)/(\text{conc. H}_2\text{CO}_3)$  at each temperature were known. Unfortunately there does not appear to be any simple way of evaluating this ratio; the conclusion of Walker and Cormack<sup>2</sup> (recently re-expressed by Johnston)<sup>3</sup> that it is less than unity at ordinary temperature is quite devoid of experimental support.<sup>4</sup> In a following section, however, it will be shown that for the purpose of the present investigation the value of the ratio is quite immaterial, since it does not enter into any of the calculations involved.

Only with regard to the heat of ionization does our lack of knowledge concerning the ratio  $(\text{conc. CO}_2)/(\text{conc. H}_2\text{CO}_3)$  cause any confusion here. For if the value of this ratio changes to any great extent within the temperature interval 0–25°, then the heat of hydration:  $-\text{CO}_2(\text{dissolved}) + \text{H}_2\text{O} = \text{H}_2\text{CO}_3$  must be considerable (either positive or negative according

<sup>1</sup> See page 1493.

<sup>2</sup> Walker and Cormack, *J. Chem. Soc.*, 77, 13 (1900).

<sup>3</sup> Johnston, *THIS JOURNAL*, 37, 2003 (1915).

<sup>4</sup> Walker, *J. Chem. Soc.*, 83, 182 (1903).

as the ratio increases or decreases). Heat produced (or absorbed) by this reaction is included in the "heat of ionization" given by the measurements of Thomsen, consequently the *true* heat of ionization may differ considerably from the value of 2800 cal. found by him. Any change in the ratio (conc.  $\text{CO}_2$ )/(conc.  $\text{H}_2\text{CO}_3$ ) within the temperature interval  $0-25^\circ$  also introduces considerable errors into the calculation of the (apparent) "heat of ionization" by means of the van't Hoff equation, as given in Table V. Nevertheless, the fact that these calculated values show satisfactory agreement for *different temperature intervals* with the experimental value of Thomsen indicates that any disturbing factors are only small—*i. e.*, that the heat of hydration is negligible and that the degree of hydration varies but slightly with temperature.

### 5. Velocity of the Hydrogen Carbonate Ion.

In order to obtain the values for  $\Lambda_\infty$  (the equivalent conductivity at infinite dilution) for carbonic acid given in Tables I-IV above, we require to know the velocities of the ions  $\text{H}^+$  and  $\text{HCO}_3^-$  at the temperatures studied.

The velocity of the hydrogen ion at  $25^\circ$  has recently been determined by the present author<sup>1</sup> and found to have the value  $347.2 \pm 0.4$ . With the aid of the temperature coefficient given by Kohlrausch<sup>2</sup> and the tables of Johnston<sup>3</sup> the probable values for the remaining temperatures may be found: at  $18^\circ$ , 313.9; at  $12.5^\circ$ , 288; and at  $0^\circ$ , 239. The accuracy of these values naturally decreases as the extrapolation interval increases, the last value may be in error by 1%.

The velocity of the hydrogen carbonate ion is not so accurately known. From conductivity measurements of sodium hydrogen carbonate solutions, Walker and Cormack<sup>4</sup> deduced the value 40.4 at  $18^\circ$ . Since, however, the highest dilution investigated was 512 liters, the error of extrapolation to infinite dilution might be appreciable.

Conductivity measurements with more dilute solutions of both sodium and calcium bicarbonates at  $25^\circ$  have been described by the author<sup>5</sup> in a previous investigation. The values for  $\text{HCO}_3^-$  obtained from the two series were 46.0 and 46.5, respectively. These figures are rendered only approximate by reason of the grade of the conductivity water employed in the dilutions (specific conductivity =  $1.10 \times 10^{-6}$  reciprocal ohms at  $25^\circ$ ), which exercised a disturbing influence upon the values obtained at high dilutions and necessitated an uncertain correction. The measurements have, therefore, been repeated with a better sample of

<sup>1</sup> Kendall, *J. Chem. Soc.*, 101, 1275 (1912).

<sup>2</sup> Kohlrausch, *Z. Elektrochem.*, 8, 290 (1902).

<sup>3</sup> Johnston, *THIS JOURNAL*, 31, 1010 (1909).

<sup>4</sup> Walker and Cormack, *Loc. cit.*

<sup>5</sup> Kendall, *Phil. Mag.*, 23, 974 (1912).

water, the experimental procedure (preparation of the solutions, estimation of their concentration, etc.) being exactly as described in the previous communication. The results are given in the following table:

TABLE VI.—SODIUM AND CALCIUM HYDROGEN CARBONATES. 25°.

NaHCO <sub>3</sub> .		$\frac{1}{2}[\text{Ca}(\text{HCO}_3)_2]$ .	
V.	Λ.	V.	Λ.
12.1	77.3	64	83.3
24.2	81.7	128	88.8
48.4	85.3	256	93.4
96.8	88.2	512	96.7
193.6	90.6	1024	99.6
387.2	92.4	2048	102.0
774.4	93.8	∞	107.7
1548.8	94.8		
3097.6	95.5		
∞	97.1		

The water employed in the dilutions possessed a specific conductivity of  $0.80 \times 10^{-6}$  reciprocal ohms at 25°. No correction has been made in the above values for the water conductivity. That this procedure leads to accurate values for bicarbonate solutions will be seen in the following paper, where it is also shown that the extent and influence of hydrolysis is inappreciable throughout the range of dilutions investigated.

The values for the equivalent conductivity at infinite dilution are derived by graphical extrapolation, according to the method of Bates.<sup>1</sup> Subtracting the figures for the cation of each series ( $\text{Na}^+ = 51.0$  and  $\frac{1}{2}\text{Ca}^+ = 61.4$ ), we obtain the values 46.1 and 46.3, respectively, for the velocity of the hydrogen carbonate ion at 25°. The mean value, 46.2, identical with that previously determined, is employed for the calculation of the velocities for the remaining temperatures, an average temperature coefficient<sup>2</sup> for the ion being assumed. The results obtained are: at 18°, 40.1; at 12.5°, 35; and at 0°, 25. The accuracy of these values is in each case commensurate with that given for the hydrogen ion at the same temperature.

The final values derived for the equivalent conductivity of carbonic acid at infinite dilution are therefore:

At 25°, 393.4; at 18°, 354.0; at 12.5°, 323; at 0°, 264. These are the figures which have been employed in Tables I–IV above.

The ionization data for carbonic acid solutions having now been established, we require to know the concentration of that solution which is in equilibrium with the carbon dioxide of the atmosphere. For this purpose it is necessary to determine two quantities—the carbon dioxide content of the atmosphere and the solubility of carbon dioxide in water.

<sup>1</sup> Bates, *THIS JOURNAL*, **35**, 519 (1913).

<sup>2</sup> Kohlrausch, *Z. Electrochem.*, **14**, 129 (1908).

## 6. The Carbon Dioxide Content of the Atmosphere.

A general impression exists that the carbon dioxide content of the atmosphere is a quantity which, although always very small, varies widely according to the conditions. Among the factors that have been mentioned as producing variations are the following:

(a) *Location*.—Land or sea, country or city, height above the ground, height above sea-level, latitude.

(b) *Time*.—Day or night, season of year, long-periodic changes.

(c) *Weather*.—Rain or fine, foggy or clear, sun or cloud, windy or calm, hot or cold.

(d) *Chance*.—Volcanic eruptions, forest fires, factory fumes, etc.

The actual effect of most of these influences is still uncertain.<sup>1</sup>

If large variations do constantly occur, then obviously it will be impossible to calculate standard values for the specific conductivity of pure water in contact with air, since the concentration of the saturated solution will vary considerably with the conditions. Nevertheless the fact that the experimentally-obtained values of different investigators in different laboratories check so remarkably closely suggests that, even in a laboratory atmosphere, any variations are in general only of minor importance.

The question of the difference between a normal out-door atmosphere and a laboratory atmosphere may first be considered. In this connection, the extensive researches of Benedict<sup>2</sup> on the oxygen content of the atmosphere afford some interesting evidence. The normal carbon dioxide content of outdoor air was found by him to be 3.1 parts in 10,000 by volume (mean of 212 analyses). Even in the Grand Central subway station of New York City, during a rush hour, the value is only doubled—6.1 parts in 10,000. Observations on the air of a crowded business street in Boston showed only the slightest trace of an increase. Hence in a well-ventilated laboratory the divergence from the normal out-door value should obviously not be excessive.

With regard to the influence of location, etc., the following quotation from a memoir by Letts and Blake<sup>3</sup> is, in view of the exhaustive nature of their tabulations, quite decisive: "It must be granted that the *average amount* of atmospheric carbonic anhydride is much the same under the most diverse conditions of weather, locality, season, etc. But on the other hand, there can be no doubt that variations in the amount do occur. These variations, if small in actual amount, are *relatively* large, and correspond with fluctuations of at least 10% of the total quantity."

<sup>1</sup> Letts and Blake, *Proc. Roy. Soc. Dublin*, 9, 107-270, 436-453 (1900).

<sup>2</sup> Benedict, "The Composition of the Atmosphere," *Publ. Carnegie Inst. Wash.*,

1912.

<sup>3</sup> Letts and Blake, *Loc. cit.*, pp. 173-4.



The present author is fortunate in being able to give direct experimental results on this important part of the problem from four laboratories situated in widely-separated localities: Edinburgh, Petrograd, Stockholm and New York City. The figures obtained are in entire agreement with the conclusions of Letts and Blake, the extreme variation in any one laboratory being  $\pm 5\%$  and for the whole range of observations being  $\pm 10\%$ . Conditions were kept as nearly constant as possible by working in large, well-ventilated rooms which contained no gas flames and were not employed for any other chemical work at the same time. The experimenter was the only person in the room and carefully abstained from smoking until determinations were completed.

Several methods were attempted for the estimation of carbon dioxide but the only simple procedure to afford rapid and consistent results was the Walker modification of the Pettenkofer method.<sup>1</sup> This gave values for the carbon dioxide content of the atmosphere which, as checked by duplicate measurements and by blank experiments, were found to be accurate to less than 0.1 part in 10,000 of the total volume. For a description of the experimental procedure and for the method of calculating the results the original paper of Walker should be consulted.

The results obtained are summarized in the following table. The values are expressed as parts of carbon dioxide in 10,000 parts by volume of air, without correction for moisture. They consequently represent partial pressures of carbon dioxide, in atmospheres multiplied by  $10^{-4}$ .

TABLE VII.—CARBON DIOXIDE CONTENT OF THE ATMOSPHERE.

Laboratory.	Time.	Number of deter- minations	Carbon dioxide. Vols. per 10,000.		
			High.	Low.	Average.
University of Edinburgh.....	March, 1911	18	3.88	3.56	3.69
Technological Institute, Petrograd...	Jan., 1913	10	3.80	3.51	3.65
Nobel Institute, near Stockholm....	June, 1913	8	3.56	3.21	3.29
Columbia University.....	July, 1915	24	3.52	3.26	3.39
		60	3.88	3.21	3.53

From an inspection of the above figures it will be evident that the variations are within the limits indicated by Letts and Blake, the greatest divergence from the final mean value—out of a total of sixty determinations—being a little less than  $\pm 10\%$ . If the results for any one laboratory only are considered, the maximum variation is in the region of  $\pm 5\%$ .

Such fluctuations are, in fact, only what may be looked for under the circumstances. The experimental method is accurate to less than 0.1 part in 10,000 of the total volume, but this represents an error of  $\pm 3\%$  in the carbon dioxide content. The tension of the water vapor in the atmosphere at the ordinary temperature of  $20^\circ$  may vary between 0 mm.

<sup>1</sup> Walker, *J. Chem. Soc.*, 77, 1110 (1900); see also Letts and Blake, *Loc. cit.*, pp. 219-229.

and 17.5 mm., *i. e.*, about 2% of the total atmospheric pressure, and since the results in Table VII are not corrected for moisture,<sup>1</sup> this involves a corresponding variation of 2% in the carbon dioxide content. The variations in the results for any one laboratory are thus practically accounted for. The larger variations in the mean value for different laboratories are in all probability due rather to small locality influences than to differences of ventilation. Thus the higher values at Edinburgh and Petrograd may be explained by the fact that the university buildings are situated in each instance near the center of the city. The Nobel Institute, on the other hand, lies out in the country several miles from Stockholm and the laboratories at Columbia are exposed to the fresh breezes across the Hudson<sup>2</sup> even in July.

As legitimately-comparable values of another observer, the results of Letts and Blake for the carbon dioxide content of "air collected in a large unused room in Queen's College, Belfast, with open windows and free circulation" may be quoted.<sup>3</sup> A total of twenty-three determinations shows the following values (expressed in parts per 10,000 by volume and not corrected for moisture): high, 3.73; low, 3.28; mean, 3.49; maximum variation,  $\pm 7\%$ .

It is evident, therefore, that the carbon dioxide content of the atmosphere of a well-ventilated laboratory, unused for other chemical work, is in all normal cases near to the average value of 3.53 parts in 10,000 by volume given in Table VII above. The deviations *may* amount to  $\pm 10\%$ . The fact may be pointed out at once, however, that such deviations will in no way vitiate the conclusions drawn in the following sections of this paper. A variation of 10% in the partial pressure of carbon dioxide involves, indeed, a variation of only 5% in the specific conductivity of the solution in equilibrium with the gas.<sup>4</sup> Variations of this magnitude are found in the observed values, as will be seen later.

In view of the relatively large errors that have been mentioned, it would be difficult to obtain a "standard value" for the carbon dioxide content of the atmosphere to a much higher degree of accuracy than the above, even if that content were (as it certainly is not) a true constant. The fact that exceedingly large variations (as much as 700%) have been recorded by numerous observers is probably due to the faulty methods of estimation that have been generally employed. The most careful and

<sup>1</sup> In order that the values shown may represent actual partial pressures of carbon dioxide.

<sup>2</sup> Also, at times, to the acid fumes from the New Jersey factories. When these were present in quantity, it was necessary to defer experimental work until the wind changed to another quarter.

<sup>3</sup> Letts and Blake, *Loc. cit.*, pp. 136-138.

<sup>4</sup> The specific conductivity varies as the square root of the partial pressure; see the following section.

recent analyses of pure out-door air indicate relatively constant values. Unfortunately most of the observations on record have been obtained in connection with nonchemical investigations, and these frequently betray the fact that at least a little knowledge of chemistry would have been of great assistance to the experimenter, both in the choice of a method and in the execution of the necessary manipulations.

### 7. The Solubility of Carbon Dioxide in Water.

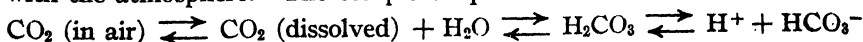
The old and approximate absorption data of Bunsen<sup>1</sup> may be discarded in favor of the more recent and accurate determinations of Bohr and Bock<sup>2</sup> and of Just.<sup>3</sup> Bohr and Bock obtained the following solubility values for the temperatures considered in this paper:

	Absorption coefficient.	Solubility in g. mols per liter.
0°	1.713	0.0764
18°	0.928	0.0414
25°	0.759	0.0338

The second column indicates the number of volumes of carbon dioxide (reduced to 0° and 760 mm.) absorbed by one volume of water at the given temperature when the partial pressure of the gas is one atmosphere (760 mm. Hg). In the third column the concentration of the saturated solution under the same conditions is shown. The values of Just are in close agreement with these.

From the above figures the concentration of the saturated solution under atmospheric conditions (carbon dioxide 3.53 parts in 10,000 by volume) can be calculated. It may be noted that variations in the atmospheric pressure—which may amount to about 3% of the total pressure, affecting the partial pressure of carbon dioxide in the same ratio—may be neglected in this calculation, owing to the greater uncertainty in the "standard value" of 3.53 parts in 10,000 for the carbon dioxide content of the atmosphere. The deviations of carbon dioxide from Boyle's law for pressures below atmospheric<sup>4</sup> may also be left out of consideration for the same reason. The partial pressure of carbon dioxide in the air may therefore be taken as equal to  $760 \times 3.53 \times 10^{-4}$  mm. Hg.

Henry's law in its simple form cannot be employed in our calculations, since at the high dilutions involved the degree of ionization of carbonic acid becomes considerable. It is here that Knox<sup>5</sup> and others have gone astray in estimating the concentration of the solution in equilibrium with the atmosphere. The complete equilibrium series:



<sup>1</sup> Bunsen, *Ann.*, 93, 1 (1855).

<sup>2</sup> Bohr and Bock, *Ann. Physik*, 44, 318 (1891).

<sup>3</sup> Just, *Z. physik. Chem.*, 37, 342 (1901).

<sup>4</sup> See Washburn, "Principles of Physical Chemistry," pp. 30-31 (1915).

<sup>5</sup> Compare Walker and Cormack, *J. Chem. Soc.*, 77, 12 (1900).

leads for dilute solutions<sup>1</sup> to the equations

conc.  $\text{CO}_2$  (in air) =  $k_1$  conc.  $\text{CO}_2$  (dissolved) =

$$k_2 \text{ conc. } \text{H}_2\text{CO}_3 = k_3 \text{ conc. } \text{H}^+ \cdot \text{conc. } \text{HCO}_3^-,$$

in which  $k_1$ ,  $k_2$  and  $k_3$  are constants for any given temperature. The fact that the nonionized solute exists partly as  $\text{CO}_2$  and partly as  $\text{H}_2\text{CO}_3$  does not complicate our calculations at all, since, as will be seen from the above equations, the ratio: (conc.  $\text{CO}_2$ )/(conc.  $\text{H}_2\text{CO}_3$ ) in dilute solutions will be a constant,  $k_2/k_1$ . The series of equilibria therefore simplifies to the following relationships:

(1)  $p/C_u = \text{constant}$ ; where  $p$  is the partial pressure of  $\text{CO}_2$ ,  $C_u$  the concentration of the *total* nonionized solute.

(2)  $C_i^2/C_u = \text{constant}$ ; where  $C_i$  is the concentration of the ionized solute.

These may be further condensed into the simple equation:  $C_i^2/p = \text{constant}$ , whence it follows that *the specific conductivity of a solution of carbonic acid is proportional to the square root of the partial pressure of carbon dioxide under which it exists*. The specific conductivities of the solutions in equilibrium with the air, in which the partial pressure of  $\text{CO}_2$  is  $3.53 \times 10^{-4}$  atmospheres, can therefore readily be obtained for the three temperatures of  $0^\circ$ ,  $18^\circ$  and  $25^\circ$  by combination of the results of Table IV with those of the present section.

For purposes of comparison, the complete solubility and ionization values for these temperatures, under partial pressures of  $\text{CO}_2$  of 1 atmosphere and  $3.53 \times 10^{-4}$  atmospheres, respectively, are given in Tables VIII and IX below. All concentrations are expressed in mols per liter.

TABLE VIII.—SOLUBILITY OF  $\text{CO}_2$  IN WATER ( $p = 1 \text{ ATM.}$ ).

T.	Conc. "total non-ionized" solute.	Conc. ionized solute.	Total concentration.	% ionization.
$0^\circ$	$7.63 \times 10^{-3}$	$1.3 \times 10^{-4}$	$7.64 \times 10^{-3}$	0.16
$18^\circ$	$4.13 \times 10^{-3}$	$1.1 \times 10^{-4}$	$4.14 \times 10^{-3}$	0.26
$25^\circ$	$3.37 \times 10^{-3}$	$1.1 \times 10^{-4}$	$3.38 \times 10^{-3}$	0.33

TABLE IX.—SOLUBILITY OF  $\text{CO}_2$  IN WATER ( $p = 3.53 \times 10^{-4} \text{ ATM.}$ ).

T.	Conc. "total non-ionized" solute.	Conc. ionized solute.	Total concentration.	% ionization.
$0^\circ$	$2.69 \times 10^{-3}$	$2.46 \times 10^{-6}$	$2.94 \times 10^{-3}$	8.4
$18^\circ$	$1.46 \times 10^{-3}$	$2.13 \times 10^{-6}$	$1.67 \times 10^{-3}$	12.8
$25^\circ$	$1.19 \times 10^{-3}$	$2.05 \times 10^{-6}$	$1.40 \times 10^{-3}$	14.7

It will be seen that the concentration of the nonionized portion of the solute decreases rapidly as the temperature rises. In the case of the ionized portion, however, the decrease is but slight, the diminution in the

<sup>1</sup> Where the partial pressure of carbon dioxide is small and the concentration the water in the solution has not been changed appreciably by the addition of the solute.

solubility being almost counterbalanced by the increase in the ionization constant. The last column shows that the degree of ionization of the saturated solution under atmospheric conditions is considerable.

### 8. The Specific Conductivity of the Saturated Solution.

The specific conductivity of pure water in equilibrium with atmospheric carbon dioxide at the temperatures of 0°, 18° and 25° can be calculated directly from the above tables. It may be noted that the specific conductivity of the water itself under these conditions becomes quite negligible in view of the relatively large hydrogen-ion concentration of the solute.

TABLE X.—CALCULATED CONDUCTIVITY OF WATER IN EQUILIBRIUM WITH CO<sub>2</sub> OF AIR.

T.	Dilution of saturated soln.	Concentration of ionized solute.	$\Delta_{\infty}$ H <sub>2</sub> CO <sub>3</sub> .	Specific conductivity.
0°	34000 liters	$2.46 \times 10^{-6}$	264.0	$0.65 \times 10^{-6}$
18°	60000 liters	$2.13 \times 10^{-6}$	354.0	$0.75 \times 10^{-6}$
25°	71400 liters	$2.05 \times 10^{-6}$	393.4	$0.80 \times 10^{-6}$

It will be seen that, while the concentration of the ionized solute decreases slowly with rise of temperature, the ionic mobilities increase at a greater rate, hence the specific conductivity of the saturated solution, as shown in the last column of the table, *increases* with the temperature. The degree of accuracy of these values, taking into account the errors inherent in the standard value for the CO<sub>2</sub> content of the atmosphere, may be stated as  $\pm 5\%$ .

We may now proceed to the final step of the investigation—the comparison of the calculated values with those obtained by direct conductivity measurements. In the following table the figures for the specific conductivities of samples of carefully purified water in equilibrium with a normal laboratory atmosphere are collected. Measurements were carried out in each of the four laboratories already mentioned, at the three temperatures of 0°, 18° and 25°. The method of preparation of the conductivity water was the same in all cases—a single distillation from ordinary tap water to which a few cubic centimeters of Nessler's solution had been added.<sup>1</sup> The water so obtained was allowed to stand exposed to the ordinary laboratory atmosphere, and, after it had rapidly come to equilibrium with this, was found to give readings which were practically independent of the time. The conditions in each laboratory during the measurements were kept as nearly as possible the same as in the determination of the carbon dioxide content of the atmosphere. The conductivity work was carried out in small cells of the Arrhenius type in the usual manner.

<sup>1</sup> The preparation of conductivity water will be found fully described in the following paper.

TABLE XI.—MEASURED CONDUCTIVITY OF WATER IN EQUILIBRIUM WITH CO<sub>2</sub> OF AIR.

Laboratory.	Specific conductivity. (Reciprocal ohms $\times 10^{-4}$ .)		
	T. = 0°.	T. = 18°.	T. = 25°.
University of Edinburgh.....	.....	0.75-0.80	0.85-0.90
Technological Institute, Petrograd.....	0.60-0.70	0.80-0.85	0.85-0.90
Nobel Institute, near Stockholm.....	.....	.....	0.75-0.80
Columbia University, New York City....	0.60-0.65	0.70-0.80	0.75-0.85

The variations in the measured values are such as would be expected from the variations in the carbon dioxide content of the different laboratories.<sup>1</sup> The concordance of the values with those calculated is extremely satisfactory, as may be seen by comparison with the figures shown in the last column of Table X. The agreement obtained is, indeed, so striking as to warrant an emphatic repetition of the conclusion drawn by Walker and Cormack from their investigations,<sup>2</sup> that "*we may assume with confidence that carbon dioxide is the only substance in the atmosphere which confers conductivity on water.*"

Supplementary evidence in confirmation of the above assertion will be found in the succeeding paper, where the conductivity measurements of other observers on carefully purified water are collected and discussed. It will also be shown that solubility and electromotive force data support the assumption that *the purest distilled water of the laboratory is, in point of fact, a saturated solution of carbonic acid under the existing atmospheric conditions.* The significance of this in the interpretation of conductivity determinations at very high dilutions will then be examined in detail for electrolytes of different types.

### 9. Summary.

Exact values have been obtained, for temperatures of 0°, 18°, and 25°, for the following quantities necessary in the calculation of the specific conductivity of pure water in equilibrium with atmospheric carbon dioxide: (a) the ionization constant of carbonic acid; (b) the mobility of the hydrogen carbonate ion; (c) the carbon dioxide content of the atmosphere; (d) the solubility of carbon dioxide in water under atmospheric conditions.

The specific conductivity of a solution of carbonic acid at any given temperature is shown to be proportional to the square root of the partial pressure of carbon dioxide under which it exists.

The values for the specific conductivity of pure water in contact with air, derived with the use of the above data, are, for each temperature considered, practically identical with the directly-measured conductivity values.

The conclusion is drawn that carefully purified conductivity water really

<sup>1</sup> Compare Table VII.

<sup>2</sup> Walker and Cormack, *J. Chem. Soc.*, 77, 12 (1900).

consists of a saturated solution of carbonic acid under the partial pressure of the carbon dioxide in the atmosphere, and contains no other conducting impurities in appreciable quantity.

In a following paper some practical applications of this result in the correction of conductivity determinations at high dilutions will be developed, and further evidence of its validity will be brought forward.

NICHOLS LABORATORIES OF INORGANIC CHEMISTRY,  
COLUMBIA UNIVERSITY, NEW YORK CITY.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW HAMPSHIRE COLLEGE.]

### THE RARE EARTH COBALTICYANIDE.

BY C. JAMES AND P. S. WILLAND.

Received June 8, 1916.

The first rare earth cobalticyanide was prepared by Cleve and Hoeglund.<sup>1</sup> In 1915 the cobalticyanides were examined during a search for a method to separate yttrium from erbium,<sup>2</sup> and owing to the facts that the separation of yttrium from erbium was rapid, and that neodymium collected in the most soluble fractions, further investigations were carried out with the following results:

**Neodymium Cobalticyanide**,  $\text{Nd}_2(\text{CoC}_6\text{N}_6)_2 \cdot 9\text{H}_2\text{O}$ .—This compound was easily precipitated from a boiling solution of neodymium chloride by adding potassium cobalticyanide. Neodymium chloride was kept in excess. The salt, which possessed a pale lilac color, formed a heavy crystalline powder. Microscopic examination showed that the crystals belong to the hexagonal system. They were almost insoluble in water, very slightly soluble in concentrated hydrochloric acid, and rapidly decomposed by boiling sodium hydroxide.

In order to determine the percentage of neodymium, some of the material was boiled with sodium hydroxide to decompose it. The hydroxide, after filtering and washing well, was dissolved in dilute hydrochloric acid and precipitated as the oxalate. This was ignited and weighed. The average for the neodymium amounted to 32.80 per cent., which seemed to indicate that the formula should be  $\text{Nd}_2(\text{CoC}_6\text{N}_6)_2 \cdot 9\text{H}_2\text{O}$ . The cobalt was determined by electrolysis after breaking up the salt by fusion with bisulfate and rendering the solution alkaline by ammonium hydroxide. The results were a little below the theoretical.

When the compound was heated it gave off water and gradually turned blue. At higher temperatures it underwent rapid decomposition with the evolution of sparks.

**Yttrium Cobalticyanide**,  $\text{Y}_2(\text{CoC}_6\text{N}_6)_2 \cdot 9\text{H}_2\text{O}$ .—This salt was prepared by precipitating a boiling solution of yttrium nitrate with a hot solution of potassium cobalticyanide.

<sup>1</sup> *Bull. soc. chim.*, — 193-201 (1873).

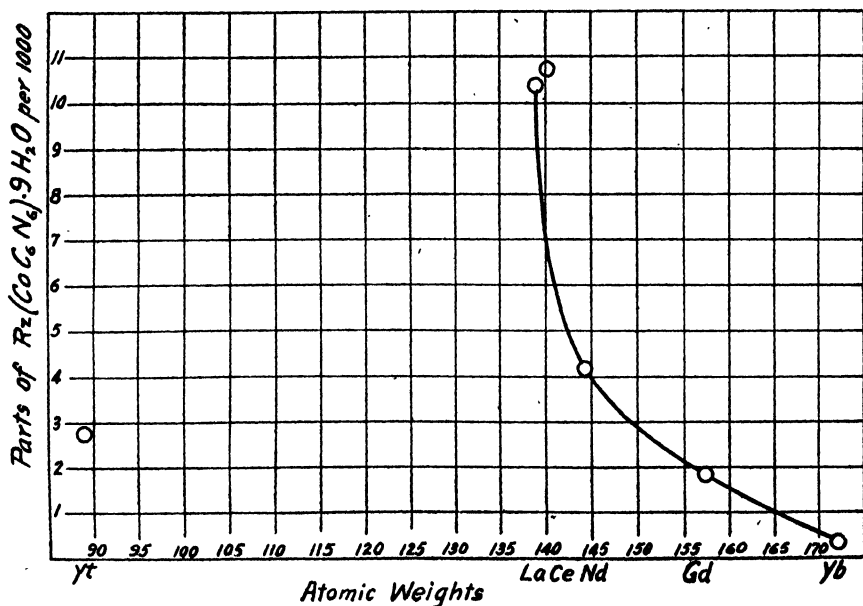
<sup>2</sup> *THIS JOURNAL*, 37, 2642 (1915).

The precipitate was crystalline and creamy white in color. It was almost insoluble in water and hydrochloric acid, but was decomposed by boiling with sodium hydroxide.

The percentage of yttrium was determined in a similar manner to that of neodymium. The yttrium found amounted to 22.95%, indicating the presence of nine molecules of water of crystallization. From this it would seem that the rare earth cobaltcyanides possess the type formula  $R_2(\text{CoC}_6\text{N}_6)_2 \cdot 9\text{H}_2\text{O}$ .

Other cobaltcyanides were prepared in a similar manner to those described above. The lanthanum salt formed a heavy precipitate consisting of hexagonal bipyramids. They were a little more soluble in water than the neodymium compound, and were somewhat soluble in concentrated hydrochloric acid. Cerium cobaltcyanide was obtained as a white crystalline precipitate with a slightly yellow tint. The solubility in water and concentrated hydrochloric acid was of about the same degree as the lanthanum salt. Gadolinium cobaltcyanide formed very quickly. The precipitate was very finely divided and almost insoluble. Ytterbium cobaltcyanide was white, crystalline and insoluble. When a solution of potassium cobaltcyanide was boiled with a solution of thorium nitrate, no precipitate formed, even though the original volume had been greatly reduced.

In order to obtain some comparison of the solubilities of these compounds, they were rotated in a thermostat with 10% hydrochloric acid. Three grams of each salt were placed in a bottle with 50 cc. of hydrochloric





acid having a sp. gr. of 1.050 at 15°. After they had rotated for two weeks at 25°, they were allowed to settle. Some of the liquid was weighed, precipitated with oxalic acid and allowed to stand fifteen hours before filtering, igniting and weighing. From these results the parts per thousand were calculated and plotted against the atomic weights.

Compound.	Atomic weight.	Parts per thousand.
$\text{La}_2(\text{CoC}_6\text{N}_6)_2 \cdot 9\text{H}_2\text{O}$ .....	139.0	10.41
$\text{Ce}_2(\text{CoC}_6\text{N}_6)_2 \cdot 9\text{H}_2\text{O}$ .....	140.25	10.75
$\text{Nd}_2(\text{CoC}_6\text{N}_6)_2 \cdot 9\text{H}_2\text{O}$ .....	144.3	4.19
$\text{Gd}_2(\text{CoC}_6\text{N}_6)_2 \cdot 9\text{H}_2\text{O}$ .....	157.3	1.86
$\text{Yb}_2(\text{CoC}_6\text{N}_6)_2 \cdot 9\text{H}_2\text{O}$ .....	172.0	0.38
$\text{Y}_2(\text{CoC}_6\text{N}_6)_2 \cdot 9\text{H}_2\text{O}$ .....	89.0	2.78

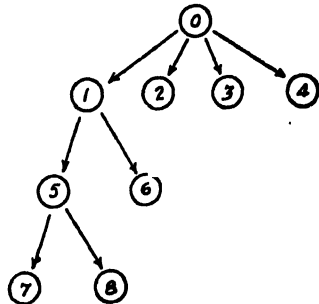
The curve obtained from the above data shows that yttrium cobalticyanide is of about the same solubility as the samarium and europium compounds, and more than three times more soluble than the erbium salt. The separation of yttrium and terbium would seem to be less efficient, since the terbium salt is about twice as soluble as that of erbium.

#### Separation of Mixed Oxides.

1. Oxides containing dysprosium, holmium, and yttrium, with traces of erbium, terbium and neodymium. These were dissolved in nitric acid, diluted to about 600 cc., boiled, and a solution of potassium cobalticyanide added until a quantity of precipitate had formed. This was filtered off and the process repeated. The precipitates were boiled with sodium hydroxide, filtered, washed and dissolved in nitric acid. The solutions were then precipitated as the oxalates, ignited and again converted into the nitrates, the solutions of which were examined by means of a spectroscope.

Fraction I showed very strong holmium and dysprosium bands and traces of neodymium and erbium. In Fraction II holmium and dysprosium were still very strong, neodymium was weak and there was a trace of erbium. Fraction III showed strong neodymium dysprosium and holmium bands. There was a slight trace of erbium. In Fraction IV, neodymium was stronger while holmium and dysprosium were weak. The material was mainly yttrium nitrate.

Fraction I was diluted, boiled and more cobalticyanide added. The precipitate that formed was filtered off and the remaining rare earth thrown out as the oxalate. These



Fractions, V and VI, were converted to the oxides. V was again dissolved in nitric acid and split into two more fractions as shown in the sketch herewith.

In color the oxides varied from a chocolate-brown to a light chamois proportional to the equivalents, showing that terbium tends to go to the least soluble end. All the oxides were boiled with water to remove any alkali metal before the equivalents were determined.

No. of fraction.	II.	III.	IV.	VI.	VII.	VIII.
Atomic weight.....	109.5	95.2	89.0	102.3	132.9	122.4

2. Separation of erbium from yttrium. The oxide used was very rich in erbium. Twenty-five grams were dissolved in hydrochloric acid, diluted to about 800 cc. and precipitated as in the case of the dysprosium, holmium and yttrium oxides. Two fractions were taken, and these, after converting to oxides and redissolving, were again fractioned. Fraction I gave Fractions III, IV and V, while Fraction II gave Fractions VI and VII. The oxides varied from a rose color to an extremely pale pink. Fraction III, the least soluble, possessed the most color, and Fraction VII, the most soluble, was the palest.

No. of fraction.	III.	IV.	V.	VI.	VII.
Atomic weight.....	142.3	137.2	127.8	110.1	93.7

The cobaltcyanide method is excellent for the separation of yttrium from erbium and *vice versa*. The precipitates are very crystalline, and the process can be quickly carried out.

One of the authors and another are investigating the ferricyanides, which are nice crystalline compounds and which differ very considerably in their solubilities. By fractionally precipitating a solution of the nitrates of yttrium and erbium with potassium ferricyanide, a rapid separation is effected.

DURHAM, N. H.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF COLUMBIA UNIVERSITY, No. 271.]

## AMMONIUM IODIDE, ITS SOLUBILITIES AND THE ABSENCE OF A TRANSITION POINT.

BY ALEXANDER SMITH AND HERBERT E. EASTLACK.

Received June 12, 1916.

Wallace<sup>1</sup> observed no irregularities in the cooling curves of ammonium iodide between 220° and -16.5°, and no change under the microscope between 16° and the sublimation point. He notes that, while the chloride and bromide crystallize in pentagonal icositetrahedra, there is some evidence that above their transition point they are cubical, just like the iodide, and the alkali iodides. He refers also to Tuton's<sup>2</sup> statement that the molecular volumes of ammonium sulfate and its double salts lie between those of rubidium and caesium, and himself found that, of the am-

<sup>1</sup> *Centr. Min.*, 1900, 33.

<sup>2</sup> *Z. Kryst.*, 38, 602 (1904); 41, 321 (1906).

monium halides, only the iodide showed this relation. Wallace concluded, therefore, that the transition point of the iodide, if there is any, must lie below  $-16.5^{\circ}$ , and that the ordinary form of the salt is the one stable above this point.

Although the transition points of the chloride and bromide are high, the transformations on cooling are sluggish. It seemed possible, therefore, that the iodide might possess a transition point below the temperature at which it is ordinarily crystallized from solution, and that, on account of the low temperature of transition, the point might have escaped notice. Definite information being necessary for other work being done in this laboratory, heating and cooling curves were made, without result. The solubility curve of ammonium iodide in water was then determined from  $-19^{\circ}$  to  $136^{\circ}$ . Except for one measurement by Eder<sup>1</sup> at  $15^{\circ}$ , and three analyses of the cryohydrate at  $-27.5^{\circ}$  by Guthrie,<sup>2</sup> the literature contains no solubility measurements with this salt. The continuity of our solubility curve shows conclusively that, at one atmosphere pressure, no transition point exists between the above-mentioned temperatures. Considering that the transition point of the chloride is higher than that of the bromide, and the comparative ease with which a transition point, if it existed, could have been observed at higher temperatures, the solubility curve of the iodide was not carried above the transition point of the bromide.

**Solubility Measurements.**—The ammonium iodide was recrystallized twice from distilled water, was washed with alcohol and ether, and was heated for ten hours at  $115^{\circ}$  in an air bath to expel volatile impurities. It was perfectly white. The method employed was identical with that used by us with ammonium bromide.<sup>3</sup> For the points below  $0^{\circ}$ , an alcohol bath, cooled by a freezing mixture, was employed. By immersing the sealed bulb containing the ammonium iodide and water, for a few seconds, in a mixture of solid carbon dioxide and ether, the minute crystals, required for determining the equilibrium points when approached from below, were obtained. Although more time was needed for reaching equilibrium at the low temperatures, the saturation temperatures could be determined  $\pm 0.5^{\circ}$ . In the tables, the solubilities are in grams of  $\text{NH}_4\text{I}$  per 100 g. water.

Eder's determination at  $15^{\circ}$  (167 g.) lies very close to our curve. Guthrie's analyses of the cryohydrate at  $-27.5^{\circ}$  are so erratic that two of his determinations fall above, while the third falls below the extension of our curve.

<sup>1</sup> *Dingler's Polytech. J.*, **221**, 189 (1876).

<sup>2</sup> *Phil. Mag.*, [4] **49**, 213 (1875).

<sup>3</sup> *THIS JOURNAL*, **38**, 1261 (1916).

TABLE I.—SOLUBILITIES OF  $\text{NH}_4\text{I}$  IN  $\text{Aq}$ —OBSERVATIONS.

Temp.	Solty.	Temp.	Solty.	Temp.	Solty.
—19°	136.7	32.2°	183.4	93.8°	243.9
—6	148.6	47.2	197.1	110.5	262.4
+6.4	160.2	55.5	204.3	135.0	292.1
10.1	163.2	61.3	210.3	136.0	294.5
25.0	176.7	70.8	219.6	.....	.....
29.6	181.2	80.8	229.3	.....	.....

TABLE II.—SOLUBILITIES OF  $\text{NH}_4\text{I}$  IN  $\text{Aq}$  AT ROUNDED TEMPS.

Temp.	Solty.	Temp.	Solty.	Temp.	Solty.
—20°	136.0	25°	176.8	80°	228.8
—10	145.0	30	181.4	100	250.3
0	154.2	40	190.5	120	273.6
10	163.2	50	199.6	140	299.2
15	167.8	60	208.9	...	.....
20	172.3	70	218.7	...	.....

**Summary.**—The solubilities of ammonium iodide have been measured between —19° and 136°.

The points lie on a single smooth curve, thus confirming Wallace's conclusion regarding the non-existence of a transition point within the same range of temperatures.

NICHOLS LABORATORIES OF INORGANIC CHEMISTRY,  
COLUMBIA UNIVERSITY, NEW YORK CITY.

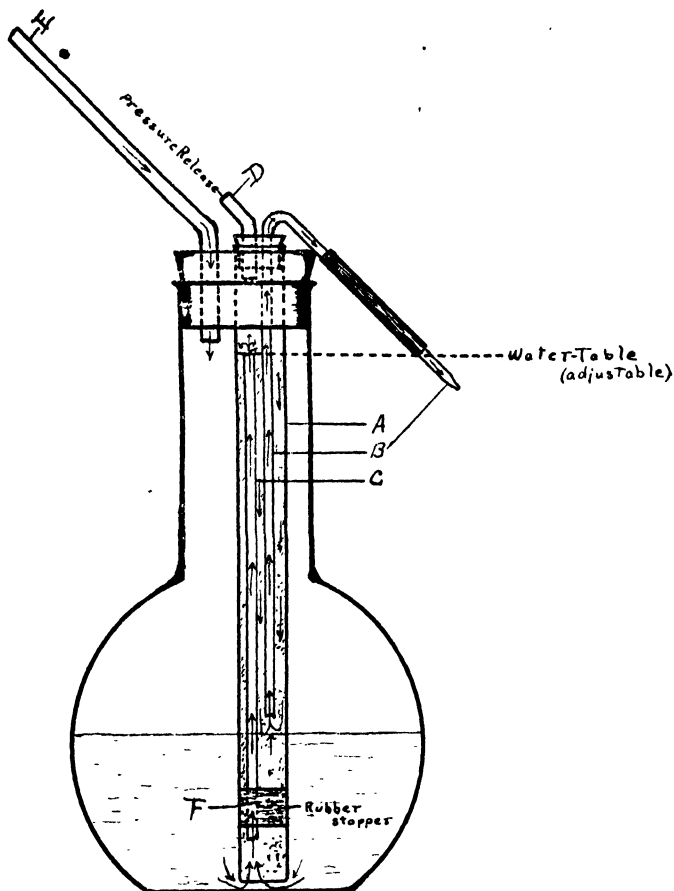
### NOTE.

**A Non-Spattering Wash Bottle.**—To avoid spattering at the tip of the nozzle of the ordinary wash bottle the principle of raising the water-table of the wash bottle slightly above the level of the tip of the nozzle has been adopted so that "back action" will not take place and the nozzle tube will remain permanently full of water.

A careful study of the diagram will make the principle clear. While in use the thumb is held over the pressure release D, the water is forced up through the tube C till the water-table indicated, has been reached, the water level being maintained by the stopper F. The nozzle works the same as though the wash bottle were full up to the raised water level. Before releasing the pressure from the mouth piece the thumb is taken off the tube D so that the height of the water-table in A may be insured and to prevent "back action" through B.

In construction the following details are important:

1. Make D 5 mm. or as large as possible to afford a quick release of pressure, having it project only to the bottom of the small cork in A.
2. The size (4 mm.) and length of B are not important just so the bottom projects an inch or so below the water-table.
3. The stopper F should be near the bottom of A for best results.



4. The tube A (12 mm.) projects up through the stopper and to the bottom of the bottle.

5. The intake C should be 4 mm. or as small as possible and still give sufficient flow. Its height determines the height of the water-table.

**Note.**—All calibrations are outside measurements. F. C. CLAPP.

DIVISION OF SOILS, MINNESOTA AGRICULTURAL EXPERIMENT STATION,  
ST. PAUL, MINNESOTA.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]  
**RELATIONS BETWEEN THE CONSTANTS OF DIBASIC ACIDS  
AND OF AMPHOTERIC ELECTROLYTES.**

BY ELLIOT QUINCY ADAMS.

Received April 4, 1916.

This paper comprises some remarks on the ionization of polybasic acids, of their acid esters, of polyacid bases, and of amphoteric electrolytes.

The fact that the two dissociation constants of a dibasic acid seldom differ by a factor *less* than four or five appears in all experimental studies of such constants,<sup>1</sup> and Walker<sup>2</sup> observed that the constants of acid esters of symmetrical dibasic acids are never<sup>3</sup> more than half those of the acids from which they are derived. In the following discussion it will be shown that these results are to be expected.

The term amphoteric is applied to two classes of compounds—hydroxyl compounds, like  $\text{Zn}(\text{OH})_2$ , which may lose either hydroxyl or hydrogen ion—and compounds like the amino acids which may gain or lose hydrogen ion; and in the latter case the practice of expressing the “base constant” of such electrolytes in terms of hydroxide ion concentration has very greatly obscured the results.<sup>4</sup>

In this paper the constants for amino acids and amines will be expressed in terms of hydrogen ion concentration, *e. g.*, for aniline<sup>5</sup>  $K = (\text{C}_6\text{H}_5\text{NH}_2) \cdot (\text{H}^+) / (\text{C}_6\text{H}_5\text{NH}_3^+)$ .

The first point to be investigated will be the relation between the two ionization constants of a dibasic acid. The ionization of such an acid is represented in Fig. 1 in which the two ionizable hydrogens are distinguished by being written, respectively, before and after the symbol A of the negative radical.  $K_1$ ,  $K_2$ ,  $K_3$ ,  $K_4$  are the respective constants for the reactions  $\text{HAH} \rightleftharpoons \text{H}^+ + \text{AH}^-$ ,  $\text{HAH} \rightleftharpoons \text{HA}^- + \text{H}^+$ ,  $\text{HA}^- \rightleftharpoons \text{H}^+ + \text{A}^{--}$ ,  $\text{AH}^- \rightleftharpoons \text{A}^{--} + \text{H}^+$ , namely,  $K_1 = (\text{H}^+)(\text{AH}^-)/(\text{HAH})$ , etc.

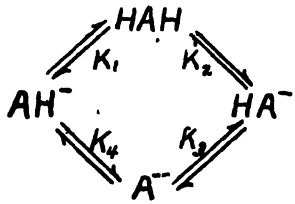


Fig. 1.

(It follows that  $K_1K_4 \equiv K_2K_3$ .)

Expressions for the first and second ionization constants as ordinarily defined,  $K'$  and  $K''$ —since  $(\text{AH}^-) + (\text{HA}^-)$  is the total concentration of intermediate ion—may be derived as follows:

$$K' = \frac{[(\text{AH}^-) + (\text{HA}^-)](\text{H}^+)}{(\text{HAH})} = K_1 + K_2 \quad (1)$$

$$K'' = \frac{(\text{A}^{--})(\text{H}^+)}{(\text{AH}^-) + (\text{HA}^-)} = \frac{1}{1/K_4 + 1/K_3} = \frac{K_3K_4}{K_3 + K_4} \quad (2)$$

From these general equations may be derived the simpler equations for certain special cases.

<sup>1</sup> Cf. E. E. Chandler, *THIS JOURNAL*, 30, 707 (1908).

<sup>2</sup> J. Walker, *J. Chem. Soc.*, 61, 715-7 (1892).

<sup>3</sup> Adipic acid (*Loc. cit.*) is only an apparent exception, for the fall in the observed constant on dilution shows clearly, as Walker himself pointed out, the presence of some conducting impurity.

<sup>4</sup> As will be shown later.

<sup>5</sup> In the following equation  $(\text{C}_6\text{H}_5\text{NH}_2)$  means the aggregate concentration of aniline and all of its hydrates, just as  $(\text{H}^+)$  means the aggregate concentration of hydrogen ion and all of its hydrates, etc.

The simplest of these is that in which the acid is symmetrical and the hydrogens independent of each other's ionization. Then  $K_1 = K_2 = K_3 = K_4 = K$  and Equations 1 and 2 become

$$K' = 2K; K'' = \frac{1}{2}K. \quad (3) (4)$$

The condition of symmetry is easily satisfied, that of adequate separation of the hydrogens not so easily, for in the "straight chain" of five or six carbon atoms ring formation is possible and hence the ends of the chain may be near one another even when no ring is formed. In the derivatives of triphenylmethane the rigidity of the benzene rings may be trusted to keep *para*-substituents in the several rings apart; and the best examples of Equations 3, 4 are found in such derivatives. Thus the two constants for phenolphthalein<sup>1</sup> as determined colorimetrically by Rosenstein<sup>2</sup> are  $K' = 11.5 \times 10^{-10}$ ,  $K'' = 2.83 \times 10^{-10}$ , whence  $K'/K'' = 4.06$ , while the first two constants of crystal violet as determined spectrophotometrically by Adams and Rosenstein<sup>3</sup> and expressed in terms of acid concentration (although crystal violet is a base) are  $1.62 \times 10^{-2}$  and  $6.6 \times 10^{-2}$ , whence  $K'/K''$  for the yellow salt, regarded as a dibasic acid, is 4.08. The extreme closeness to 4 is accidental, as the ratio, in the second case at least, is uncertain to five per cent. or more.

Chandler<sup>4</sup> has shown that the ratio of the constants for dibasic organic acids approaches this value at high concentrations.

For *independently* ionizable hydrogens in an unsymmetrical acid  $K_3 = K_1$ ,  $K_4 = K_2$  and Equation 2 becomes

$$K'' = \frac{K_1 K_2}{K_1 + K_2}. \quad (5)$$

If the hydrogens are not sufficiently separated to ionize independently, we may generalize from the behavior of oxalic acid and its immediate homologs, whose first constants are markedly greater and whose second constants are distinctly less than the ionization constants of the corresponding fatty acids; and state the principle that a negative group in-

<sup>1</sup> Un-ionized phenolphthalein and its singly charged ion are colorless, and are therefore supposed to be entirely in the lactone form; the doubly charged ion is pink and consists of a mixture, in tautomeric equilibrium, of the ion of colorless phenolphthalein and that of an unsymmetrical quinoid phenol-acid,  $O:C_6H_4:C(C_6H_4OH)-C_6H_4CO_2H$ . Since the ratio of the two constants, determined experimentally, agrees with that for a symmetrical dibasic acid, the quinoid ion can constitute only a few per cent., at most, of the tautomeric mixture.

<sup>2</sup> I. Rosenstein, *THIS JOURNAL*, **34**, 1117 (1912); cf. phenol,  $K = 1.1 \times 10^{-10}$ .

<sup>3</sup> E. Q. Adams and I. Rosenstein, *THIS JOURNAL*, **36**, 1452 (1914). In crystal violet the quinoid basic group is not involved in the change from the violet to the green and yellow forms. The two remaining nitrogens are equivalent, hence the yellow ion is symmetrical with respect to the two hydrogens which it is able to lose.

<sup>4</sup> E. E. Chandler, *THIS JOURNAL*, **30**, 707 (1908).

creases and a negative charge diminishes the ionizability of any hydrogen in the molecule, whence  $K_3 < K_1$ ,  $K_4 < K_2$  and Equation 2 becomes

$$K'' < \frac{K_1 K_2}{K_1 + K_2} \quad (6)$$

Dividing (1) by (6)

$$\frac{K'}{K''} > \frac{(K_1 + K_2)^2}{K_1 K_2} > \frac{(K_1 + K_2)^2}{K_1 K_2} - \frac{(K_1 - K_2)^2}{K_1 K_2}$$

but

$$\frac{(K_1 + K_2)^2}{K_1 K_2} - \frac{(K_1 - K_2)^2}{K_1 K_2} = \frac{4K_1 K_2}{K_1 K_2} = 4,$$

whence

$$\frac{K'}{K''} > 4. \quad (7)$$

That is to say, the first ionization constant will in general be more than four times<sup>1</sup> the second, the limiting ratio of 4 being found in *symmetrical* acids whose hydrogens are widely separated (and, therefore, *independently ionizable*).

For a *tribasic* acid it may be shown in similar fashion that the limiting ratio between successive constants is 3; indeed the calculation may be made for an acid with any number of hydrogens.

The truth of the conclusion for dibasic acids may be seen in Table I. The data are taken, unless otherwise indicated from Scudder,<sup>2</sup> and are, in general, at 25°.

The acid esters of dibasic acids will differ from the acids in two ways: by the loss of one hydrogen and by the effect on the other hydrogen of the substitution. If the second effect—which will be in general a decrease in the “polar character” of the molecule and, therefore, of the ionization—be neglected, then, as Wegscheider<sup>3</sup> showed, the ionization constant for the *acid ester* of a *symmetrical* dibasic acid will be one-half the first constant of the acid, and the *sum* of the constants for the two isomeric acid esters of an *unsymmetrical* dibasic acid will be *equal* to the first constant of the acid. Table II shows in how far this expectation is borne out.

To amphoteric electrolytes Equations 1, 6 and 7 derived above, apply directly if the constant of the basic part of the molecule be expressed in terms of hydrogen ion concentration. Much of the supposedly anomalous behavior of amphoteric electrolytes is due to the neglect of the possibility that the constants so expressed will be related in such a

<sup>1</sup> Cf. E. E. Chandler, *Loc. cit.*

<sup>2</sup> Scudder, “The Electrical Conductivity and Ionization Constants of Organic Compounds,” Van Nostrand (1914).

<sup>3</sup> R. Wegscheider, *Monatsh. Chem.*, 16, 153 (1895).



TABLE I.

Acid.	K'.	K''.	K'/K''.
(CO <sub>2</sub> H) <sub>2</sub> .....	0.10	4.9 × 10 <sup>-5</sup>	2000
CH <sub>2</sub> (CO <sub>2</sub> H) <sub>2</sub> .....	1.6 × 10 <sup>-3</sup>	2.0 × 10 <sup>-6</sup>	800
(CH <sub>2</sub> ) <sub>2</sub> (CO <sub>2</sub> H) <sub>2</sub> .....	6.8 × 10 <sup>-5</sup>	2.7 × 10 <sup>-6</sup>	25
(CH <sub>2</sub> ) <sub>3</sub> (CO <sub>2</sub> H) <sub>2</sub> .....	4.7 × 10 <sup>-5</sup>	2.9 × 10 <sup>-6</sup>	16.2
(CH <sub>2</sub> ) <sub>4</sub> (CO <sub>2</sub> H) <sub>2</sub> .....	3.6 × 10 <sup>-5</sup>	2.8 × 10 <sup>-6</sup>	12.9
(CH <sub>2</sub> ) <sub>5</sub> (CO <sub>2</sub> H) <sub>2</sub> .....	3.4 × 10 <sup>-5</sup>	2.6 × 10 <sup>-6</sup>	13.1
(CH <sub>2</sub> ) <sub>6</sub> (CO <sub>2</sub> H) <sub>2</sub> .....	3.0 × 10 <sup>-5</sup>	2.3 × 10 <sup>-6</sup>	13.0
(CH <sub>2</sub> ) <sub>7</sub> (CO <sub>2</sub> H) <sub>2</sub> .....	2.7 × 10 <sup>-5</sup>	2.4 × 10 <sup>-6</sup>	11.3
(CH <sub>2</sub> ) <sub>8</sub> (CO <sub>2</sub> H) <sub>2</sub> .....	2.6 × 10 <sup>-5</sup>	2.6 × 10 <sup>-6</sup>	10.0
H(CH <sub>2</sub> ) <sub>7</sub> CO <sub>2</sub> H.....	1.4 × 10 <sup>-5</sup>		
<i>cis</i> -C <sub>2</sub> H <sub>2</sub> (CO <sub>2</sub> H) <sub>2</sub> .....	1.3 × 10 <sup>-2</sup>	4.6 × 10 <sup>-7</sup>	50000
<i>trans</i> -C <sub>2</sub> H <sub>2</sub> (CO <sub>2</sub> H) <sub>2</sub> .....	1.0 × 10 <sup>-3</sup>	2.2 × 10 <sup>-6</sup>	45
<i>o</i> -C <sub>6</sub> H <sub>4</sub> (CO <sub>2</sub> H) <sub>2</sub> .....	1.2 × 10 <sup>-3</sup>	3.1 × 10 <sup>-6</sup>	390
<i>m</i> -C <sub>6</sub> H <sub>4</sub> (CO <sub>2</sub> H) <sub>2</sub> .....	2.9 × 10 <sup>-4</sup>	2.4 × 10 <sup>-5</sup>	12
C <sub>8</sub> H <sub>14</sub> (CO <sub>2</sub> H) <sub>2</sub> .....	2.3 × 10 <sup>-5</sup>	0.7 × 10 <sup>-6</sup>	33
<i>cis</i> - <i>p</i> -C <sub>6</sub> H <sub>10</sub> (CO <sub>2</sub> H) <sub>2</sub> .....	3.0 × 10 <sup>-5</sup>	3.0 × 10 <sup>-6</sup>	10
<i>trans</i> - <i>p</i> -C <sub>6</sub> H <sub>10</sub> (CO <sub>2</sub> H) <sub>2</sub> .....	4.6 × 10 <sup>-5</sup>	2.5 × 10 <sup>-6</sup>	18
<sup>9</sup> H <sub>2</sub> SO <sub>4</sub> .....	0.45	1.7 × 10 <sup>-2</sup>	26
<sup>9</sup> H <sub>2</sub> SO <sub>4</sub> .....	1.7 × 10 <sup>-2</sup>	5.0 × 10 <sup>-6</sup>	3400
<sup>9</sup> H <sub>2</sub> CO <sub>3</sub> .....	3.0 × 10 <sup>-7</sup>	1.3 × 10 <sup>-11</sup>	23000

way that the constant determined in acid solution is the acid constant and that in alkaline solution the basic constant.

Aminoacetic acid, for example, has the constants  $K_A = 1.8 \times 10^{-10}$ ,  $K_B = 2.8 \times 10^{-12}$ , which become in the notation used in this article  $K'' = 1.8 \times 10^{-10}$ ,  $K' = \frac{1.0 \times 10^{-14}}{K_B} = 3.7 \times 10^{-3}$ , which are to be

compared with the constants for methylamine  $K = \frac{1.0 \times 10^{-14}}{4.1 \times 10^{-14}} = 2.4 \times 10^{-11}$ , N-benzoyl aminoacetic acid,  $K = 2.2 \times 10^{-4}$ , acetic acid,  $K = 1.8 \times 10^{-5}$ , N-acetyl aminoacetic acid,  $K = 2.3 \times 10^{-4}$ , chloroacetic acid,  $K = 1.6 \times 10^{-3}$ , showing that aminoacetic acid is at once an acid stronger than monochloroacetic acid and a base nearly as strong as methylamine.

<sup>1</sup> By inversion; by partition =  $4.4 \times 10^{-6}$ .

<sup>2</sup> By inversion; by conductivity =  $1.9 \times 10^{-6}$ ; by partition =  $3.7 \times 10^{-6}$ .

<sup>3</sup> By conductivity; by partition =  $3.3 \times 10^{-6}$ .

<sup>4</sup> By conductivity; by partition  $2.0 \times 10^{-7}$ ; by inversion  $3.9 \times 10^{-7}$ ,  $5.5 \times 10^{-7}$ .

<sup>5</sup> By partition and inversion; by conductivity  $3.0 \times 10^{-6}$ .

<sup>6</sup> By partition; by conductivity  $3.9 \times 10^{-6}$ ; by inversion  $1.7 \times 10^{-6}$ ,  $2.2 \times 10^{-6}$ .

<sup>7</sup> By conductivity; by partition  $2.7 \times 10^{-6}$ ; by inversion  $1.0 \times 10^{-6}$ .

<sup>8</sup> These values are given for *d*-, *l*-, and *dl*-camphoric acids. Chandler (*Loc. cit.*) gives for the second constant of *d*-camphoric acid (by conductivity)  $K'' = 14 \times 10^{-8}$ , but he uses  $K' = 2.3 \times 10^{-4}$  in his calculations (apparently by mistake). As camphoric acid is an unsymmetrical acid it was rather surprising to find for it constants whose ratio is less than 2.

<sup>9</sup> Landolt-Börnstein Tabellen (1912 edition).

TABLE II.  
 Symmetrical Acids.

Acid.	K'.	Ester.	K.
$\text{CH}_2(\text{CO}_2\text{H})_2$ .....	$1.6 \times 10^{-3}$	Ethyl	$0.46 \times 10^{-3}$
$(\text{CH}_3)_2(\text{CO}_2\text{H})_2$ .....	$6.8 \times 10^{-6}$	Methyl	$3.2 \times 10^{-5}$
		Ethyl	$3.0 \times 10^{-5}$
$(\text{CH}_3)_4(\text{CO}_2\text{H})_2$ .....	$4.2 \times 10^{-5}$	Ethyl	$2.5 \times 10^{-5}$
$(\text{CH}_3)_6(\text{CO}_2\text{H})_2$ .....	$3.0 \times 10^{-6}$	Ethyl	$1.5 \times 10^{-5}$
$(\text{CH}_3)_8(\text{CO}_2\text{H})_2$ .....	$2.8 \times 10^{-6}$	Ethyl	$1.4 \times 10^{-5}$
<i>cis</i> - $\text{C}_2\text{H}_2(\text{CO}_2\text{H})_2$ .....	$1.3 \times 10^{-2}$	Ethyl	$0.11 \times 10^{-2}$
<i>trans</i> - $\text{C}_2\text{H}_2(\text{CO}_2\text{H})_2$ .....	$1.0 \times 10^{-3}$	Ethyl	$0.48 \times 10^{-3}$
<i>o</i> - $\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$ .....	$1.2 \times 10^{-3}$	Methyl	$0.66 \times 10^{-3}$
		Ethyl	$0.55 \times 10^{-3}$
<i>d</i> -( $\text{CHOHC}_2\text{H}_4$ ) $_2$ .....	$9.7 \times 10^{-4}$	Methyl	$4.6 \times 10^{-4}$
$(\text{CH}_3)_3\text{C}(\text{CO}_2\text{H})_2$ .....	$7.6 \times 10^{-4}$	Methyl	$3.1 \times 10^{-4}$
<i>m</i> -( $\text{CHCH}_3\text{CO}_2\text{H}$ ) $_2$ .....	$1.4 \times 10^{-4}$	Methyl	$0.45 \times 10^{-4}$
<i>dl</i> -( $\text{CHCH}_3\text{CO}_2\text{H}$ ) $_2$ .....	$2.1 \times 10^{-4}$	Methyl	$0.6 \times 10^{-4}$
3,6- $\text{Cl}_2\text{C}_6\text{H}_3(\text{CO}_2\text{H})_2(1,2)$ .....	$3.4 \times 10^{-2}$	Ethyl	$1.5 \times 10^{-2}$

## Unsymmetrical Acids.

Acid.	K'.	Ester.	K <sub>1</sub> .	K <sub>2</sub> .
$\text{C}(\text{CH}_3)_2\text{CH}_2(\text{CO}_2\text{H})_2$ .....	$8.0 \times 10^{-5}$	Methyl	$2.3 \times 10^{-5}$	$2.6 \times 10^{-5}$
3- $\text{NO}_2\text{C}_6\text{H}_3(\text{CO}_2\text{H})_2(1,2)$ .....	$1.3 \times 10^{-2}$	Methyl	$1.7 \times 10^{-3}$	$0.3 \times 10^{-2}$
4- $\text{NO}_2\text{C}_6\text{H}_3(\text{CO}_2\text{H})_2(1,2)$ .....	$7.7 \times 10^{-3}$	Methyl	$3.0 \times 10^{-3}$	$5.2 \times 10^{-3}$
2- $\text{NO}_2\text{C}_6\text{H}_3(\text{CO}_2\text{H})_2(1,4)$ .....	$1.9 \times 10^{-2}$	Methyl	$0.08 \times 10^{-2}$	$2.0 \times 10^{-2}$
2- $\text{BrC}_6\text{H}_3(\text{CO}_2\text{H})_2(1,4)$ .....	$6.2 \times 10^{-3}$	Methyl	$0.37 \times 10^{-3}$	$5.0 \times 10^{-3}$
4-( $\text{OH}$ ) $\text{C}_6\text{H}_3(\text{CO}_2\text{H})_2(1,2)$ .....	$1.2 \times 10^{-3}$	Methyl	$0.15 \times 10^{-3}$	$0.20 \times 10^{-3}$
2-( $\text{OH}$ ) $\text{C}_6\text{H}_3(\text{CO}_2\text{H})_2(1,4)$ .....	$2.7 \times 10^{-3}$	Methyl	$0.25 \times 10^{-3}$	$2.77 \times 10^{-3}$
<i>o</i> - $\text{C}_6\text{H}_4(\text{CO}_2\text{H})(\text{CH}_2\text{CO}_2\text{H})$ ...	$1.9 \times 10^{-4}$	Methyl	$0.43 \times 10^{-4}$	$0.76 \times 10^{-4}$
		Ethyl	$0.46 \times 10^{-4}$	$0.71 \times 10^{-4}$
(3,4)( $\text{CH}_2\text{O}$ ) $_2\text{C}_6\text{H}_2(\text{CO}_2\text{H})_2(1,2)$ .....	$1.17 \times 10^{-3}$	Methyl	$0.17 \times 10^{-3}$	$1.30 \times 10^{-3}$
		Ethyl	$0.15 \times 10^{-3}$	$1.01 \times 10^{-3}$
		Propyl	$0.15 \times 10^{-3}$	$0.93 \times 10^{-3}$

Since K' is several million times as great as K", and is unquestionably the measure of the ionization of the carboxyl, aminoacetic acid will be almost exclusively the "inner salt,"  $\text{N}^+\text{H}_3\text{CH}_2\text{CO}_2^-$ , with less than one part per million of true amino acid,  $\text{NH}_2\text{CH}_2\text{CO}_2\text{H}$ . In the case of the aminobenzoic acids (see below) this fraction becomes about 1%. It should be pointed out that aminoacetic acid appears to be an exception to the general rule that a negative charge diminishes the ionization of any hydrogen in the molecule, for whereas acetic acid,  $\text{CO}_2\text{HCH}_3$ , loses its hydrogen more readily than acid malonate ion,  $\text{CO}_2\text{HCH}_2\text{CO}_2^-$ , methylammonium ion,  $\text{N}^+\text{H}_3\text{CH}_3$ , loses hydrogen ion less readily than aminoacetic acid,  $\text{H}^+\text{N}_3\text{CH}_2\text{CO}_2^-$ . The aminobenzoic acids do not show this anomaly, for, as bases, they are stronger than aniline.

<sup>1</sup> The data are from Scudder, but the designations  $\alpha$  and  $\beta$  have been interchanged in the case of the methyl and propyl esters to agree with Wegscheider, as Scudder quotes Wegscheider and assigns no reason for the changes.

Comparing the aminobenzoic acids with benzoic acid,  $K = 6.7 \times 10^{-5}$  and aniline  $K = 1.0 \times 10^{-14}/4.6 \times 10^{-10} = 2.2 \times 10^{-5}$ , and with their respective N-acetyl derivatives:

Acid.	$K_B = 1.0 \times 10^{-14}/K'$	$K'$	$K_A = K''$	$K(\text{acetyl-})$
<i>o</i> -Aminobenzoic.....	$1.37 \times 10^{-12}$	$7.3 \times 10^{-3}$	$1.1 \times 10^{-5}$	$2.4 \times 10^{-4}$
<i>m</i> -Aminobenzoic.....	$1.22 \times 10^{-11}$	$0.82 \times 10^{-3}$	$1.6 \times 10^{-5}$	$0.85 \times 10^{-4}$
<i>p</i> -Aminobenzoic.....	$2.33 \times 10^{-12}$	$4.3 \times 10^{-3}$	$1.2 \times 10^{-5}$	$0.52 \times 10^{-4}$
Chloroacetic acid.....	.....	$1.6 \times 10^{-3}$	.....	.....
<i>m</i> -Toluidine.....	$5.8 \times 10^{-10}$	.....	$1.7 \times 10^{-5}$	.....
<i>p</i> -Toluidine.....	$1.8 \times 10^{-10}$	.....	$0.56 \times 10^{-5}$	.....

the meta-acid is thus slightly weaker than monochloroacetic acid, the ortho- and para-acids stronger, while as bases all three lie between *m*- and *p*-toluidine, the ortho-acid being twice as strong a base as aniline.

The strongly *negative* character of the  $\text{NH}_2$  group may also be seen in the antagonistic action of neighboring  $\text{NH}_2$  groups.

	$K_B = K_w/K$	$K'$		$K_1 = K_w/K''$	$K''$
$^1\text{NH}_3$	$1.8 \times 10^{-5}$	$55. \times 10^{-11}$	$\text{N}_2\text{H}_4$	$3. \times 10^{-6}$	$300. \times 10^{-11}$
$\text{C}_2\text{H}_5\text{NH}_2$	$5.6 \times 10^{-4}$	$1.8 \times 10^{-11}$	$^3(\text{CH}_2)_2(\text{NH}_2)_2$	$0.85 \times 10^{-4}$	$11.8 \times 10^{-11}$
$\text{C}_2\text{H}_7\text{NH}_2$	$4.7 \times 10^{-4}$	$2.1 \times 10^{-11}$	$(\text{CH}_2)_3(\text{NH}_2)_2$	$3.5 \times 10^{-4}$	$2.9 \times 10^{-11}$
$^2\text{iso-C}_4\text{H}_9\text{NH}_2$	$3.1 \times 10^{-4}$	$3.2 \times 10^{-11}$	$(\text{CH}_2)_4(\text{NH}_2)_2$	$5.1 \times 10^{-4}$	$2.0 \times 10^{-11}$
$^2\text{iso-C}_8\text{H}_{11}\text{NH}_2$	$5.0 \times 10^{-4}$	$2.0 \times 10^{-11}$	$(\text{CH}_2)_8(\text{NH}_2)_2$	$7.3 \times 10^{-4}$	$1.4 \times 10^{-11}$

### Summary.

1. For polybasic acids the ionization constants  $K'$  and  $K''$  as ordinarily defined are related to the constants,  $K_1$ ,  $K_2$ , for the separate removal of the respective hydrogens, thus:

$$K' = K_1 + K_2 \quad (1)$$

$$K'' < \frac{K_1 K_2}{K_1 + K_2}, \quad (6)$$

whence

$$\frac{K'}{K''} > 4. \quad (7)$$

2. Phenolphthalein and crystal violet give values for this ratio very near the limiting value. (At high concentrations of dibasic organic acids, E. E. Chandler has shown that this same limit is approached.)

3. The acid esters of a symmetrical dibasic acid have constants equal to approximately one-half the first constant of the acid, while the sum of the constants of the isomeric esters of an unsymmetrical dibasic acid is approximately equal to the first constant of the acid. (This generalization is due to Wegscheider.)

<sup>1</sup> Not given in Scudder.

<sup>2</sup> Normal amine not given.

<sup>3</sup> For ethylenediamine  $K' = 1.0 \times 10^{-14}/6.0 \times 10^{-7} = 1.7 \times 10^{-8}$ ; for the others it is not given. It is to be remembered that a larger constant means a stronger acid or a weaker base.

4. The constants of aminoacetic acid and the aminobenzoic acids are explained by the strong *negative* character of the  $\text{NH}_2$  group.

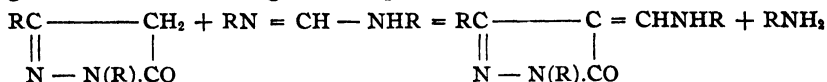
**BERKELEY, CAL.**

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF KANSAS.]  
ON THE REACTIONS OF THE FORMAMIDINES. V. ON SOME  
PYRAZOLONE DERIVATIVES.

By F. B. DAINS, H. R. O'BRIEN AND C. L. JOHNSON.

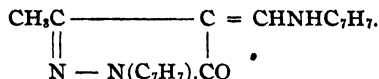
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This is a continuation of a previous investigation on the pyrazolones,<sup>1</sup> where it was shown that the methylene group in this class of derivatives reacted with the formamidines, the hydrogen being replaced by the group  $>\text{CHNHR}$ . The general equation can be formulated as follows,



the reaction yielding a substituted 4-amino methylene pyrazolone and the free amine. The following paper includes further experimental evidence as to the general nature of this reaction and a partial study of the action of certain reagents upon the substituted pyrazolones.

**4-*m*-Toluido-methylene-1-*p*-tolyl-3-methyl-5-pyrazolone,**



Molar quantities of the pyrazolone and di-*m*-tolyl formamidine were heated for twenty minutes in an oil bath at 150°. From the reaction product the new compound was isolated after treatment with dilute hydrochloric acid, which removed *m*-toluidine. This separated from alcohol in golden yellow crystals melting at 122°.

Calc. for  $C_{19}H_{19}ON_3$ : N, 13.78%. Found, 13.85%.

Under like conditions the pyrazolone and di-*o*-tolyl formamidine gave 4-*o*-toluido-methylene-1-*p*-tolyl-3-methyl-5-pyrazolone, yellow needles from alcohol which melt at 176.5°.

Calc. for  $C_{19}H_{19}ON_3$ : N, 13.78%. Found: 13.86%, 13.69%.

The ease of reaction of different formamidines seems to vary greatly. While many require heating at 120–150° in order to ensure condensation, others unite at much lower temperature. Thus *p*-tolyl methyl pyrazolone and di-*o*-phenetidyl formamidine at water-bath temperature gave the amine and 1-*p*-tolyl-3-methyl-4-*o*-ethoxyanilido-5-pyrazolone. It crystallizes from alcohol in canary-yellow needles with a melting point of 133°. The same reaction occurs slowly when the components are ground together in a mortar and allowed to stand.

<sup>1</sup> Dains and Brown, *THIS JOURNAL*, 31, 1153 (1909).

Calc. for  $C_{20}H_{21}O_2N_2$ : N, 12.54%. Found: 12.80%.

In some cases a secondary reaction was found to occur, which resulted in the formation of varying amounts of a bispyrazolone.

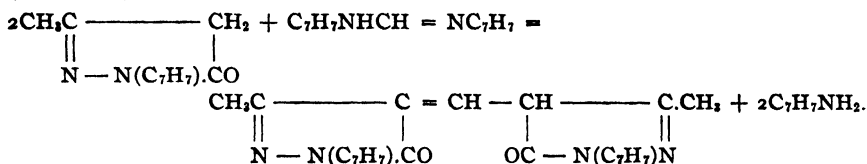
Thus the above pyrazolone and di-*p*-bromo-diphenyl formamidine gave on heating 1-*p*-tolyl-3-methyl-4-*p*-bromo-anilido-methylene-5-pyrazolone, yellow crystals from alcohol with a melting point of 196–7°.

Calc. for  $C_{18}H_{16}O_3MgBr$ : Br, 21.60%. Found: 21.29%.

In addition there is formed a bromine-free compound, difficultly soluble in alcohol, which crystallizes from chloroform in orange needles, melting at 249°. It gave on analysis the figures demanded for methenyl-bis-methyl-*p*-tolyl-pyrazolone.

Calc. for  $C_{22}H_{22}O_2N_4$ : N, 14.51%. Found: 14.77%, 14.78%.

This constitution was confirmed by the fact that the same methenyl bispyrazolone was obtained, together with *m*-toluidine, when di-*m*-tolyl formamidine (one mol) was heated with the methyl *p*-tolyl pyrazolone (two mols).



Analogous results were obtained in one experiment when a mixture of *o*-tolyl-3-methyl-5-pyrazolone and di-*p*-chloro-diphenyl formamidine was heated. Besides *p*-chloro-aniline, the only product isolated was methenyl-bis-1-*o*-tolyl-3-methyl-5-pyrazolone, which crystallizes from alcohol in orange-colored needles, melting at 190°.

Calc. for  $C_{22}H_{22}O_2N_4$ : N, 14.51%. Found: 14.75%.

The same product is obtained when the methyl-tolyl-pyrazolone is heated with orthoformic ester at 120°, thus showing the analogy in behavior of this class of compounds with both orthoformic ester and the formamidines.<sup>1</sup>

Another method of obtaining these derivatives is to heat an anilido-methylene-pyrazolone with an unsubstituted pyrazolone. Thus anilido-methylene-methyl-phenyl-pyrazolone and the methyl-phenyl-pyrazolone yield aniline and the bispyrazolone.

**1-*o*-Tolyl-3-methyl-5-pyrazolone and the Formamidines.**—Instead of simply fusing the components alone in an oil bath, in the following cases, it was found that better and cleaner yields of the amino-methylene derivatives were obtained when the substances were heated in a high boiling solvent such as xylene or kerosene. In this way the following were synthesized:

<sup>1</sup> THIS JOURNAL, 31, 1153 (1909).

1-*o*-Tolyl-3-methyl-4-anilido-methylene-5-pyrazolone, reddish brown crystals from alcohol, which melt at 140°.

Calc. for  $C_{18}H_{17}ON_3$ : N, 14.43%. Found: 14.14%, 14.43%.

1-*o*-Tolyl-3-methyl-4-*m*-xylylido-5-pyrazolone, yellow needles, melting point, 232°.

Calc. for  $C_{20}H_{21}ON_3$ : N, 13.09%. Found: 13.29%, 13.19%.

1-*o*-Tolyl-3-methyl-4-*o*-ethoxyanilido-methylene-5-pyrazolone, yellow crystals from alcohol which melt at 160°.

Calc. for  $C_{20}H_{21}O_2N_3$ : N, 12.53%. Found: 12.64%.

1-*o*-Tolyl-3-phenyl-5-pyrazolone, which was made from *o*-tolyl hydrazine and benzoyl-acetic ethyl ester, was found to react with the same ease with the substituted formamides, a fact illustrated by the following preparations.

1-*o*-Tolyl-3-phenyl-4-anilido-methylene-5-pyrazolone, from the pyrazolone and di-phenyl formamidine in boiling xylene solution, crystallizes from alcohol in light yellow needles, which melt at 169°.

Calc. for  $C_{22}H_{19}ON_3$ : N, 11.90%. Found: 11.92%, 11.87%.

The same pyrazolone and di-*m*-xylyl formamidine gave 1-*o*-tolyl-3-phenyl-4-*m*-xylylido-methylene-5-pyrazolone, yellow crystals also from alcohol, melting point 142°.

Calc. for  $C_{22}H_{23}ON_3$ : N, 11.02%. Found: 11.16%, 11.40%.

1-*o*-Tolyl-3-phenyl-4-*p*-chloroanilido-methylene-5-pyrazolone, yellow crystals which melt at 181°.

Calc. for  $C_{23}H_{17}ON_3Cl$ : N, 11.34%. Found: 11.05%, 11.12%.

Derivatives of 1-phenyl-3-methyl-5-pyrazolone. This reacts at water-bath temperature with di-*o*-ethoxyphenyl formamidine, yielding 1-phenyl-3-methyl-4-*o*-ethoxyanilido-methylene-5-pyrazolone, yellow needles which melt at 170°.

Calc. for  $C_{19}H_{19}O_2N_3$ : N, 13.09%. Found: 13.23%.

1-Phenyl-3-methyl-4-*m*-xylylidomethylene-5-pyrazolone, golden yellow needles difficultly soluble in alcohol, melting at 173°.

Calc. for  $C_{19}H_{19}ON_3$ : N, 13.65%. Found: 13.63%, 13.77%.

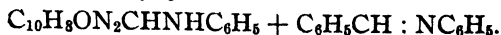
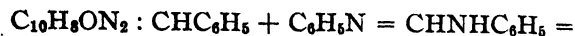
It has been shown that not only do compounds with a methylene group-  
ing react with the formamides, but also that their aldehyde condensa-  
tion products in some cases behave in a similar manner. Thus 4-benzal-  
3-methyl-isoxazolone unites with the formamides yielding benzal aniline  
and the amino-methylene derivatives much more readily and smoothly  
than does the free methyl isoxazolone.<sup>1</sup>

This same fact holds true in the case of the aldehyde condensation  
products of the pyrazolones. When 4-benzal or anisal-1-phenyl-3-  
methyl-5-pyrazolone is heated with diphenyl formamidine,<sup>2</sup> there is ob-

<sup>1</sup> Dains and Griffin, *THIS JOURNAL*, 35, 962 (1913).

<sup>2</sup> *Ibid.*, 31, 1153 (1909).

tained benzal aniline and 4-anilido-methylene-methyl-phenyl-pyrazolone, m. p. 154°.



Tambor<sup>1</sup> obtained from piperonal and methyl-phenyl-pyrazolone (equal mols), the red piperonal-methyl-phenyl-pyrazolone (m. p. 166–7°), while piperonal (one mol) and the pyrazolone (two mols) gave piperonal-di-(methyl-phenyl-pyrazolone), a white compound melting at 143°. Repeating this work it was found that the white piperonal-dipyrazolone has the higher melting point of 163°. This was heated with diphenyl formamidine with the hope of replacing the  $C_6H_5N$  < rest with two pyrazolone groups. This aim was not realized, the reaction product yielding aniline, anilido-methylene-methyl-phenyl-pyrazolone (m. p. 154°) and the red piperonal pyrazolone. The white piperonal-dipyrazolone evidently dissociates into the simple pyrazolone and the red aldehyde condensation product.

**The Action of the Amino-methylene-pyrazolones with Various Reagents. Hydrochloric Acid.**—The amino-methylene derivatives are capable of forming hydrogen chloride addition products, stable in benzene, though decomposed by water. Thus dry HCl gas precipitates from a benzene solution of 1-phenyl-3-methyl-4-*m*-xylidomethylene-5-pyrazolone a white hydrochloride melting at 189–90°.

Calc. for  $C_{19}H_{19}ON_2HCl$ : HCl, 10.67%. Found: 10.73%.

In like manner, dry hydrogen chloride gas, when passed into a benzene solution of anilido-methylene-methyl-phenyl-pyrazolone, gave a white HCl addition product, melting and decomposing at 186°.

However, if the anilido compound is boiled in an alcoholic solution of hydrochloric acid, decomposition ensues with the formation of aniline and varying but small amounts of methenyl-bismethyl-phenyl-pyrazolone (m. p. 180°).

Similar results were obtained on hydrolysis with potassium hydroxide. For instance, 4-anilido-methylene-1-*o*-tolyl-3-phenyl-5-pyrazolone was heated for a few minutes with alcoholic potash. On examination the reaction mixture was found to contain aniline and a product which separated from gasoline in orange-yellow crystals, melting at 179°. This was identified as methenyl-4-4-bis-1-*o*-tolyl-3-phenyl-5-pyrazolone, which was also readily prepared by heating the pyrazolone (two mols) with ortho-formic ester (one mol) at 120°. It is difficultly soluble in alcohol.

Calc. for  $C_{33}H_{28}O_2N_4$ : N, 10.98%. Found: 11.00%, 11.20%.

**The Action of Nitric Acid.**—To a cooled solution of anilido-methylene-methyl-phenyl-pyrazolone in concentrated sulfuric acid, was added nitric

<sup>1</sup> Ber., 33, 869 (1900).

acid (one mol sp. gr. 1.42). The product obtained by pouring the mixture into cold water was practically insoluble in alcohol, chloroform or gasoline. It was purified by recrystallization from pyridine. From this solvent it separates in brownish yellow needles, which char between 255–265°. It is unaffected by boiling hydrochloric acid under ordinary conditions, but at 150° in a sealed tube some *p*-nitro-aniline was obtained. Analysis gave discordant figures, indicating that it was a mixture of nitro products in which both the phenyl group of the ring and the side chain were nitrated.

For comparison two derivatives were prepared with a nitro group in the side chain. Phenyl-methyl-pyrazolone condenses with di-*m*-nitro-diphenyl-formamidine in boiling kerosene solution yielding 1-phenyl-3-methyl-4-*m*-nitro-anilido-methylene-5-pyrazolone, yellow needles from alcohol melting at 175°.

Calc. for  $C_{17}H_{14}O_3N_4$ : N, 17.40%. Found: 17.23%.

The corresponding 1-phenyl-3-methyl-4-*p*-nitro-anilido-methylene-5-pyrazolone separates from alcohol in orange-yellow needles which melt at 170°.

Calc. for  $C_{17}H_{14}O_3N_4$ : N, 17.40%. Found: 17.63%.

**The Action of Bromine.**—The synthesis of the amino-methylene compounds by the action of aniline on ethoxy-methylene-aceto acetic ester and of the formamidines on the benzal derivatives of the isoxazolones and pyrazolones shows that they possess the constitution  $>C = CHNHR$ . At the same time, the mechanism of the reaction by which there is formed from them pyrazol and isoxazol compounds and their behavior with bromine prove that they also exist and react in the tautomeric form<sup>1</sup>  $>CHCH = NR$ . This latter form is capable of adding two atoms of bromine and this addition product under the influence of solvents may either lose its bromine entirely or may undergo rearrangement yielding a mono-bromo substitution product and hydrogen bromide. Thus the bromine derivatives of anilido-methylene-methyl-isoxazolone and of anilido-methylene-cyanacetic ester rearrange to the corresponding *p*-bromo-anilido compounds.<sup>2</sup> 4-Anilido-methylene-1-*o*-tolyl-3-phenyl-5-pyrazolone (one mol) was dissolved in glacial acetic acid and bromine (one mol) added. On standing a heavy yellow crystalline precipitate was formed. This was purified by washing with acetic acid and drying on a porous plate in a desiccator. It melted at 238°.

Calc. for  $C_{22}H_{19}ON_2Br_2$ : Br, 31.17%. Found: 31.05%, 31.58%.

When this dibromide is dissolved in alcohol it undergoes a change, and a new compound containing only one atom of bromine results. It melted at 143° and proved to be identical with the 4-*p*-bromoanilido-methylene-3-phenyl-1-*o*-tolyl-5-pyrazolone. This was also synthesized by heating

<sup>1</sup> *Ann.*, 297, 33 (1897); *THIS JOURNAL*, 31, 1155 (1909); 35, 962, 965 (1913).

<sup>2</sup> *THIS JOURNAL*, 35, 963 (1913).



the pyrazolone and di-*p*-bromo-diphenyl formamidine in kerosene solution. It forms blunt yellow needles, easily soluble in alcohol, melting at 142–3°.

Calc. for  $C_{22}H_{18}ON_2Br$ : N, 9.73%. Found: 9.50%, 10.04%.

For the sake of comparison the corresponding 4-*m*-bromoanilido-methylene-3-phenyl-1-*o*-tolyl-5-pyrazolone was prepared from the pyrazolone and di-*m*-bromodiphenyl formamidine. This is a yellow crystalline compound, that melts at 148–50°, but is not identical with the product obtained from the dibromide.

A yellow dibromide is readily formed when bromine is added to a glacial acetic acid solution of 4-*o*-ethoxyanilido-methylene-1-phenyl-3-methyl-5-pyrazolone. It melts at 203°.

Calc. for  $C_{18}H_{19}O_2N_3Br_2$ : Br, 33.11%. Found: 32.89%, 32.84%.

When this dibromide is crystallized from alcohol, a product separates in orange-yellow needles, that is bromine-free and melts at 179°.

Calc. for  $C_{21}H_{18}O_2N_4$ : N, 15.64%. Found: 15.45%.

The nitrogen corresponds to that required for methenyl-bis-methyl-phenyl-pyrazolone and it was readily identified as that compound.

This unexpected result may be due to the action of hydrobromic acid in the alcohol solution on the anilido compound, since it has been shown earlier in the paper that hydrochloric acid may react with this type of derivatives giving the methenyl-bis-pyrazolones.

This same type of reaction occurred in another instance. Thus in the repetition of a previous experiment when 1-*o*-tolyl-3-phenyl-4-anilido-methylene-5-pyrazolone was dissolved in chloroform and bromine (one mol) added, no precipitate was formed but on evaporating the solvent a yellow bromine addition product was obtained that melted at 238°. When this was treated with alcohol and pyridine a bromine-free compound resulted, which proved to be methenyl-bis-1-*o*-tolyl-3-phenyl-5-pyrazolone (m. p. 181°) identical with the product obtained from *o*-formic ester and the pyrazolone.

**1-*p*-Bromophenyl-3-phenyl-5-pyrazolone.**—When benzoyl acetic ester and the bromophenyl hydrazine are dissolved in alcohol and warmed, there is formed the above pyrazolone. This crystallizes from alcohol in white needles melting at 154–5°.

Calc. for  $C_{18}H_{11}ON_2Br$ : Br, 25.39%. Found: 25.13%.

This compound shows the same general reactions as do the other pyrazolones with free methylene groups. Thus, heated at 120° with benzaldehyde, it yields a brilliant scarlet 4-benzal derivative, which is practically insoluble in the ordinary solvents but dissolves slightly in pyridine but does not melt at 265°.

Calc. for  $C_{22}H_{18}ON_2Br$ : Br, 19.85%. Found: 19.84%, 19.73%.

Heated in kerosene solution at  $125^{\circ}$ , the bromo-diphenyl pyrazolone and diphenyl-formamidine give aniline and 1-*p*-bromophenyl-3-phenyl-4-anilidomethylene-5-pyrazolone, which crystallizes from alcohol in fine, yellow needles, melting point  $188^{\circ}$ .

Calc. for  $C_{22}H_{16}ON_3Br$ : Br, 19.11%. Found: 19.44%.

The methenyl-bis-1-*p*-bromophenyl-3-phenyl-5-pyrazolone results from the interaction of orthoformic ester and the pyrazolone. It crystallizes in reddish yellow needles from pyridine in which it is difficultly soluble. In other solvents it is practically insoluble. It does not melt at  $265^{\circ}$ .

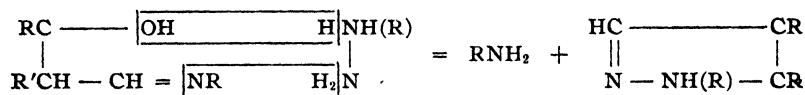
Calc. for  $C_{31}H_{20}O_2N_4Br_2$ : Br, 25.00%. Found: 24.87%.

### Pyrazole Synthesis.

It has been shown that anilido-methylene derivative of the type

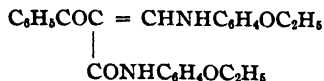
$$\begin{array}{c} \text{RC} = \text{O} \\ | \\ \text{R}'\text{C} = \text{CHNHR} \end{array}$$

react in their tautomeric forms with hydrazines yielding substituted pyrazoles as follows:<sup>1</sup>



Additional evidence for this reaction is afforded in the following experiments: *o*-Ethoxy-anilido-methylene-acetoacetic ester and phenyl hydrazine react at water-bath temperature yielding the ethyl ester of 1-phenyl-5-methyl-4-pyrazol-carboxylic ester.<sup>2</sup> The same anilido-methylene compound was heated in alcohol solution with hydrazine sulfate (with the addition of enough alkali to give the free hydrazine). The pyrazol ester first formed was saponified, since there was obtained an acid melting at  $228^{\circ}$ , evidently identical with the 4-methyl-pyrazol-3(5)-carboxylic acid described by Pechmann and Burkhard.<sup>3</sup> They give a melting point of  $218-20^{\circ}$ . However, this condensation with hydrazine alone is being further investigated.

The ethyl ester of benzoyl-acetic acid combines at water-bath temperature with di-*o*-phenetidyl-formamidine to form the *o*-ethoxyanilide of *o*-ethoxyanilido-methylene-benzoyl acetic acid.



The white crystals from alcohol melt at  $173^{\circ}$ .

Calc. for  $C_{28}H_{28}O_4N_2$ : N, 6.51%. Found: 6.91%.

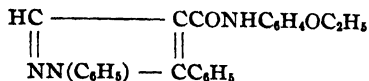
When this anilide is heated with phenyl hydrazine at  $120^{\circ}$ , phenetidine

<sup>1</sup> THIS JOURNAL, 31, 1153 (1909).

<sup>2</sup> Claisen, *Ann.*, 275, 312 (1897).

<sup>3</sup> *Ber.*, 33, 3593 (1900).

is eliminated and there is formed the *o*-ethoxyanilide of 1,5-diphenyl-4-pyrazol-carboxylic acid.



This separated from dilute alcohol in fine needles melting at 118°.

Calc. for  $\text{C}_{24}\text{H}_{21}\text{O}_2\text{N}_3$ : N, 10.97%. Found: 10.54%.

In the course of this investigation several compounds have been prepared, which will be briefly described, as they are not mentioned in the literature.

Di-*o*-phenetidyl formamidine and malonic ester at water-bath temperature gave a good yield of *o*-ethoxyanilido-methylene-diethyl-malonate,  $\text{C}_2\text{H}_5\text{OC}_6\text{H}_4\text{NHCH.C} = (\text{COOC}_2\text{H}_5)_2$ , long needles from 60% alcohol with a melting point of 66–7°.

Calc. for  $\text{C}_{16}\text{H}_{21}\text{O}_6\text{N}$ : N, 4.54%. Found: 4.63%.

1-*o*-Tolyl-3-methyl-4-monobromo-5-pyrazolone is formed when bromine (one mol) is added to a solution of the pyrazolone in glacial acetic acid. The yellow crystals from alcohol melt at 116°.

Calc. for  $\text{C}_{11}\text{H}_{11}\text{ON}_2\text{Br}$ : Br, 29.81%. Found: 30.13%, 29.99%.

1-*o*-Tolyl-3-phenyl-4-monobromo-5-pyrazolone, made in a like manner, crystallizes from alcohol in brownish yellow needles with a melting point of 110°.

Calc. for  $\text{C}_{16}\text{H}_{13}\text{ON}_2\text{Br}$ : Br, 24.29%. Found: 24.44%, 24.54%.

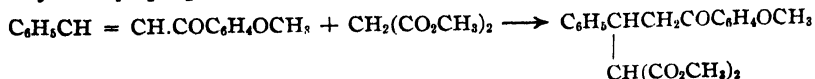
LAWRENCE, KANSAS.

## THE REACTIONS OF SOME CARBOXYL DERIVATIVES OF TRIMETHYLENE.<sup>1</sup>

By DOROTHY A. HAHN.

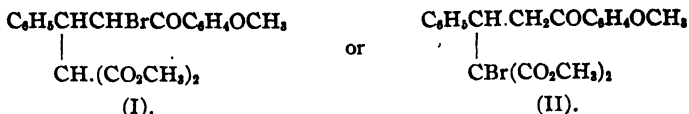
Received June 3, 1916.

The principal object of this investigation was the study of the products obtained by eliminating hydrobromic acid from bromine substitution products of the esters of anisoyl-phenyl-ethyl-malonic acid. These esters are easily obtained by adding the corresponding malonic esters to phenyl-anisyl-propenone:

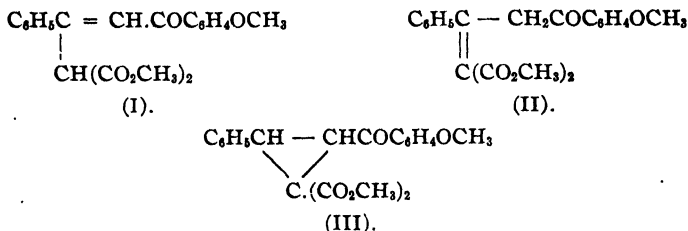


They contain one hydrogen atom that is very readily replaced by bromine; the resulting bromine substitution product may be either

<sup>1</sup> Part of a dissertation presented to the Faculty of the Graduate School of Yale University, 1916, in candidacy for the degree of Doctor of Philosophy. The work, suggested by Prof. Elmer P. Kohler of Harvard, was done at Mount Holyoke College, and was accepted at Yale upon recommendation of Prof. Treat B. Johnson.

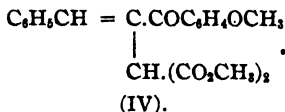


By cautious treatment with bases it is possible to remove hydrobromic acid from the bromine compound without hydrolyzing much of the ester, the yield being 80 to 87% of bromine-free ester. The main product of this process was always a substance melting at 86°, although an isomeric substance melting at 82° was sometimes obtained in sufficient quantity for separation. For products obtained in this way three formulas are possible.

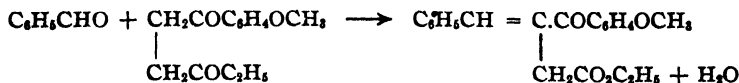


Between these formulas it is possible to decide by means of the following transformations:

When the ester melting at 86° is treated with alcoholates it forms a metallic derivative that on acidification gives an isomeric ester melting at 82°. This on further action of the same reagent passes into another metallic derivative that yields a third isomer melting at 112°. The structure of this third ester must be represented by the formula



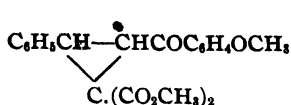
This follows from the fact that on hydrolysis and loss of carbon dioxide, it passes into an acid that can be made synthetically by condensing benzaldehyde with ethyl-β-anisoyl-propionate, and hydrolyzing the product.



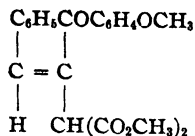
The structure of substances obtained by this reaction was established by Borsche.<sup>1</sup>

From this transformation of the ester melting at 86° into a substance with the formula represented by IV, it follows that the former must be a trimethylene compound, and that the relations between the three isomers is represented by the formulas

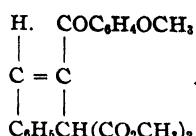
<sup>1</sup> *Ber.*, 47, 1112 (1914).



I (86°).



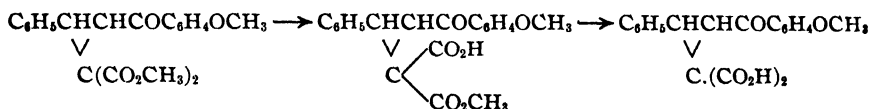
II (82°).



III (112°).

All the properties of these three isomers support this conclusion. The substances melting at 82 and 112° readily reduce permanganate while the ester melting at 86° does not. They also, as would be expected, form highly colored metallic derivatives from which they are regenerated by acids, a process that is impossible with the trimethylene compound. That the esters melting at 82 and 112° are stereoisomers is shown also by the fact that the former passes into the latter under the influence of sunlight.

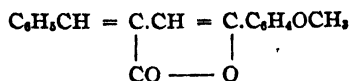
By using aqueous alkalis or alcoholates under special conditions it is possible to hydrolyze the trimethylene compound to the corresponding ester-acid, and then to the dibasic acid.



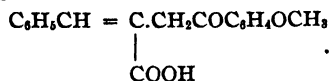
This was established by esterifying the resulting acids with methyl alcohol and hydrochloric acid—the product in each case being the ester melting at 86°. The trimethylene ring in these acids is not sensitive to bases as it is in the ester, but it opens readily on heating. Thus when the dibasic acid was heated at about 200° it lost carbon dioxide and gave a mixture of products from which four substances, two neutral and two acid, were readily separated. The neutral substances were found to be a green and a yellow unsaturated lactone, so closely related as to suggest geometrical isomerism. The green lactone is the labile form and in recrystallizing from all solvents about one-third passes over into the yellow modification. Both substances dissolve in chloroform and ethyl acetate to give deep red solutions; and in acetone, alcohol and ether to give pale yellow or greenish yellow solutions. The green lactone in solution in acetone reduces permanganate instantly, the yellow lactone does not. Both substances, when dissolved in methyl alcoholic potassium hydroxide and acidified, yield a monobasic unsaturated acid, melting at 165°. This acid, when dissolved in methyl alcohol saturated with hydrogen chloride, passes quantitatively into the yellow lactone.

Both the green and yellow lactones have been obtained by heating a mixture of  $\beta$ -anisoyl-propionic acid, benzaldehyde, and acetic anhydride. As this reaction according to Borsche<sup>1</sup> should give a lactone with the structure

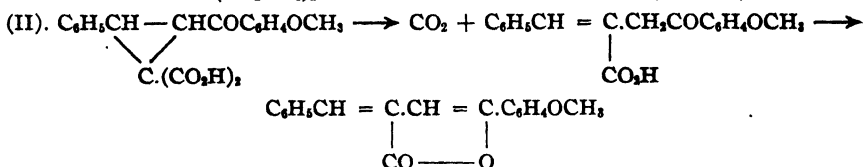
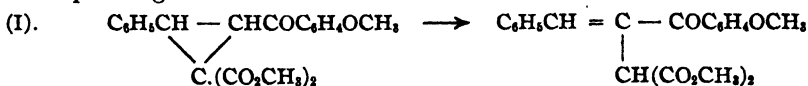
<sup>1</sup> Ber., 47, 1114 (1914).



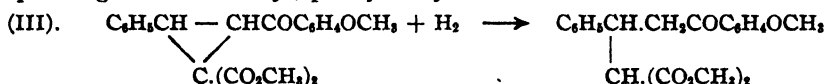
this formula must represent the isomeric green and yellow lactones; and the corresponding acid must be  $\alpha$ -benzal- $\beta$ -anisoyl-propionic acid,



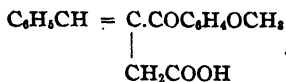
It is noteworthy that when the dibasic acid is heated, the ring opens to some extent in a different place from that in which it opens when the corresponding ester is treated with an alcoholate:



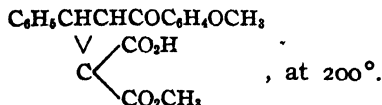
The ring may be opened in still another way. When the ester melting at  $86^\circ$ , in solution in acetic acid, was reduced with zinc dust, the corresponding ester of anisoyl, phenyl-ethylmalonic acid was obtained:



The acid products obtained as a result of heating the dibasic acid were monobasic acids, melting, respectively, at  $124$  and  $198^\circ$ . The acid melting at  $124^\circ$  was identified as  $\beta$ -benzal- $\beta$ -anisoyl-propionic acid,



It was obtained both as free acid, and as the sodium salt, and was synthesized by the method mentioned in an earlier part of this paper.<sup>1</sup> Both acid and salt reduce potassium permanganate in aqueous solution. The oxidation was attended by the formation of benzaldehyde, and the products of the reaction were identified as benzoic and anisic acids. The acid melting at  $198^\circ$  was obtained only in small quantity. When esterified with methyl alcohol and hydrochloric acid, it gives a solid ester which is identical with one of the products obtained by heating the ester acid,



<sup>1</sup> *Ber.*, 47, 1112 (1914).

### Experimental.

When dimethyl  $\beta$ -anisoyl- $\alpha$ -phenyl ethylmalonate was dissolved in chloroform and treated with a molecular equivalent of bromine, a reaction took place with the evolution of hydrobromic acid, the bromine disappearing as rapidly as added. The chloroform was distilled under diminished pressure and the oily residue dissolved in alcohol. This on evaporation deposited an oil; and all efforts to obtain a solid bromine substitution product failed. The oil, when treated with reagents such as potassium methylate, alcoholic potassium hydroxide, and magnesium methylate, yielded a number of solid isomeric products, which crystallized readily. Three substances melting at 86, 82 and 112° were separated.

The primary product obtained from the bromine derivative of methyl  $\beta$ -anisoyl- $\alpha$ -phenyl-ethylmalonate was a bromine-free ester melting at 86°. Difficulties were experienced in getting good percentage yields of this substance, because of the ease with which it is isomerized in solution. In the first experiments potassium hydroxide was used as the reagent for eliminating hydrobromic acid. An alcoholic solution of the oil obtained in the reaction between methyl anisoyl-phenyl-ethylmalonate and bromine was treated with a 10% solution of potassium hydroxide in equal parts of methyl alcohol and water, the base was added slowly, and the reaction was complete when a yellow color and an alkaline solution remained for a moment after vigorous shaking. The methyl alcohol was then removed by distillation, the residue taken up with ether, and washed with water until free from alcohol. The addition of a few crystals of ester to the dried ethereal solution caused the precipitation of a large part of the ester in almost pure form. In the absence of seed, the separation of a solid product may take place immediately, or it may be necessary to wait weeks for spontaneous crystallization in the resulting oil. The yield of pure solid varied between 30 and 60%. A better average yield was obtained by substituting magnesium methylate for potassium hydroxide. The magnesium compound was added directly to an alcoholic solution of the oil obtained by the action of bromine on methyl anisoyl-phenyl-ethylmalonate. The addition of the base was attended by a change in color varying from salmon to red. Part of the alcohol was removed immediately by distillation and the residue was decomposed with aqueous hydrochloric acid and extracted with ether. The ethereal solution, when washed and dried over calcium chloride, yielded an average of 60 to 70% pure crystalline ester. In all experiments the separation of a solid product was greatly interfered with by the presence of a thick, yellow oil. Residues consisting of this oil deposited additional small quantities of crystals very slowly. The method finally used was a modification of the second and eliminated extraction with ether. 100 g. of

methyl anisoyl-phenyl-ethylmalonate were dissolved in chloroform and treated with 45 g. of bromine. The chloroform was immediately distilled from a water bath under diminished pressure, and the residue, while still hot, was dissolved in a solution of magnesium methylete, prepared by adding 8 g. of magnesium to 200 cc. of alcohol. The magnesium compound was added slowly, with constant shaking, and its addition was attended by an evolution of heat, and by marked changes in color to green, yellow, orange, and finally deep red. A series of parallel experiments showed that the ultimate color of the solution did not influence in any apparent way the quantity nor the quality of the product. The separation of a solid crystalline substance began almost immediately, and was complete within 4 to 12 hrs.; and the yield varied between 82 and 87% of almost pure ester, melting at 82–84°. It was purified by recrystallization from ether.

0.1540 g. subs. and 0.1452 g. subs. gave 0.3866 and 0.3646 g.  $\text{CO}_2$  and 0.0718 and 0.0641 g.  $\text{H}_2\text{O}$ .

Calc. for  $\text{C}_{21}\text{H}_{20}\text{O}_6$ : C, 68.4%; H, 5.4%. Found: C, 68.4, 68.4; H, 5.1, 4.9.

The substance is very soluble in ether acetone, and hot alcohol, slightly soluble in cold alcohol and ligroin. The ester melting at 86° does not reduce permanganate. In solution in carbon tetrachloride it slowly decolorizes bromine with the evolution of hydrobromic acid. Ten grams of substance reacted readily with an equivalent of bromine, but the resulting oil showed no tendency to crystallize even after standing for months. Dissolved in glacial acetic acid and treated with zinc dust and a small quantity of water, the substance passed quantitatively into methyl- $\gamma$ -anisoyl- $\beta$ -phenyl-ethylmalonate.

Under the proper conditions the ester may be hydrolyzed to an ester acid and then to a dibasic acid.

**Methyl Potassium 1-Phenyl-2 Anisoyl Trimethylene Dicarboxate (3-3).**—The pure ester melting at 86° may be hydrolyzed to a neutral monopotassium salt by adding exactly one equivalent of potassium hydroxide to a solution of the ester in five times its weight of methyl alcohol. The base was added slowly as a 25% solution in equal parts of methyl alcohol and water; and the mixture became neutral upon standing from 10 to 12 hrs. in an ice-chest. Since there was no separation of solid product upon standing, the solution was concentrated by evaporation on a water bath. Addition of a small quantity of ether to the cooled solution caused the immediate precipitation of a white crystalline solid.

0.1054, 0.1023 and 0.1025 g. subs. gave 0.0221, 0.0218 and 0.0217 g.  $\text{K}_2\text{SO}_4$ .

Calc. for  $\text{C}_{20}\text{H}_{17}\text{O}_6\text{K}$ : K, 9.94%. Found: K, 9.39, 9.55, 9.49.

The salt is readily soluble in water and in alcohol, insoluble in ether.



It was recrystallized from alcohol-ether mixtures, from which it separates in glistening<sup>a</sup> plates that melt at 152°. At about 170° the substance changes color to a reddish brown and a little above this temperature decomposition with the rapid evolution of CO<sub>2</sub> takes place. When acidified in aqueous solution it gives an oily precipitate which slowly solidifies. When purified this was found to consist of a monobasic acid melting at 162°.

**Methyl-1-phenyl-2-anisoyl-trimethylene Dicarmonic Acid.**—The ester-acid may be prepared by acidifying an aqueous solution of the pure potassium salt; or by hydrolyzing the ester melting at 86° with one equivalent of potassium hydroxide and, after allowing the mixture to stand overnight in a cool place, acidifying with hydrochloric acid. The oil precipitating from acid solution was taken up by chloroform, washed and dried over calcium chloride. The acid crystallizes from chloroform on evaporation, or on the addition of a small quantity of ligroin.

0.1484 and 0.1572 g. subs. gave 0.3674 and 0.3903 g. CO<sub>2</sub>; and 0.0690 and 0.0680 g. H<sub>2</sub>O.

Calc. for C<sub>20</sub>H<sub>18</sub>O<sub>6</sub>: C, 67.7%; H, 5.08%. Found: C, 67.5, 67.7; H, 5.1, 4.8.

The substance crystallizes in large, white prisms, that melt at 162°, and that decompose with the evolution of CO<sub>2</sub> at about 200°. It is very soluble in chloroform, ethyl acetate, and acetone, soluble in ether, and insoluble in ligroin. It may be most readily separated from small quantities of the dibasic acid, occurring as impurities, by recrystallization from chloroform-ligroin mixtures. The basicity of the substance was determined by titration. When dissolved in alcohol and hydrolyzed in the presence of an excess of potassium hydroxide, the acid ester passes into a dipotassium salt, which on acidification gives a dibasic acid, melting at 192°. In alcoholic solutions saturated with hydrogen chloride, it passes quantitatively into the dimethyl ester, melting at 86°. When heated at about 200° the ester-acid loses CO<sub>2</sub>. The reddish brown mass obtained as the result of this action was poured into ether and the ethereal solution was extracted with sodium carbonate. The product was found to be neutral in character. When a small quantity of ligroin was added to the washed and dried ethereal solution, a substance separated slowly, in the form of fine needles or plates. This on recrystallization from ether-ligroin mixtures and finally from methyl alcohol melted at 121°. It was identified as the ester of an acid melting at 198°. The filtrates from which this solid separated were evaporated to dryness on a water bath and were treated with a solution of potassium hydroxide in methyl alcohol. The alkaline solution on dilution with a large quantity of water remained clear, and on acidification with hydrochloric acid, precipitated an oil which slowly solidified. This was found to consist almost entirely of an acid melting at 147° and identified as  $\beta$ -anisoyl-propionic acid.

**Dipotassium 1-Phenyl-2-Anisoyl-trimethylene Dicarbonate (3-3).—**

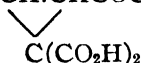
This substance was obtained by hydrolyzing the ester melting at  $86^{\circ}$  in alcoholic solution with an excess of concentrated aqueous potassium hydroxide. The base was added slowly with constant shaking to the cooled solution of the ester and the salt separated almost immediately in the form of white, glistening plates. It was filtered and washed first with a small quantity of alcohol and then with acetone.

0.1320 g. subs. and 0.1140 g. subs. gave 0.0551 g. and 0.0477 g. of  $K_2SO_4$ .

Calc. for  $C_{19}H_{14}O_6K_2$ : K, 18.7%. Found: K, 18.7, 18.6.

The substance is very soluble in water, sparingly soluble in alcohol and almost insoluble in acetone. Its aqueous solution gave, on acidification, a white, oily precipitate, which slowly solidified, and which consisted of a dibasic acid, melting at  $192^{\circ}$ .

**1 - Phenyl - 2 - anisoyl - trimethylene Dicarmonic Acid (3-3).—**  
 $C_6H_5CH.CHCOC_6H_4OCH_3$ , was obtained by hydrolyzing the dimethyl



ester melting at  $86^{\circ}$  and the ester acid melting at  $162^{\circ}$ , in the presence of excess of concentrated aqueous potassium hydroxide, and acidifying the product. It was also obtained, along with other substances, when the two dimethyl esters, isomeric with the ester melting at  $86^{\circ}$ , were hydrolyzed with potassium hydroxide. Finally it was obtained by the hydrolysis of the corresponding ethyl esters. The oil which separated on acidifying the aqueous solution of the dipotassium salt of this acid, was allowed to solidify, and then washed and dried. It was extracted repeatedly with small quantities of chloroform to remove any acid ester present as impurity, washed once with a very small quantity of ether, and recrystallized from ethyl acetate, or from acetic acid. The pure substance melted at  $192^{\circ}$ , changed in color to a golden brown at about this temperature and at about  $200^{\circ}$  decomposed with the rapid evolution of  $CO_2$ .

0.1497 g. and 0.1226 g. subs. gave 0.3680, 0.3008 g.  $CO_2$ ; and 0.0623, 0.0519 g.  $H_2O$ .

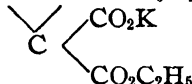
Calc. for  $C_{19}H_{16}O_6$ : C, 67.0; H, 4.7. Found: C, 67.0, 66.9; H, 4.6, 4.7.

The substance is sparingly soluble in water from which it separates slowly in crystalline form. It is very soluble in acetic acid, acetone and ethyl acetate, 1 pt. by weight of substance dissolving in 4, 4, and 14 pts., by weight of these respective solvents. It is slightly soluble in ether, almost insoluble in chloroform, and insoluble in ligroin. It is most readily recrystallized from ethyl acetate-ligroin mixtures from which about 90% of the dissolved substance separates upon cooling. The basicity of the acid was determined by titration with standard alkali. In solution in carbon-bisulfide the substance reacts readily with a molecular equivalent

of bromine with the evolution of hydrobromic acid, but no solid was separated from the resultant oil. In solution in methyl alcohol saturated with hydrogen chloride, the acid passes readily into the methyl ester melting at  $86^{\circ}$ . Heated above  $200^{\circ}$  the acid decomposes with the evolution of carbon dioxide. Two neutral and two acid products were obtained as a result of this decomposition, which will be considered later on in this paper.

**1-Phenyl-2-anisoyl-trimethylene Dicarmonic Acid (3-3)** was also obtained by hydrolyzing the corresponding monoethyl ester. The diethyl ester was never isolated, so that a description of this ester-acid and its salt may be considered at this point.

**Ethyl Potassium 1-Phenyl-2-anisoyl Trimethylene Dicarboxate (3-3)**,  $C_6H_5CH-CHCOC_6H_4OCH_3$ , was obtained by treating diethyl ( $\beta$ -bromo- $\beta$ -



anisoyl- $\alpha$ -phenyl-ethyl) malonate<sup>1</sup> in alcoholic solution with two equivalents of potassium hydroxide. The alkali was added as a 25% solution in equal parts of alcohol and water, and the mixture was allowed to stand overnight. The solution was then concentrated and allowed to cool when a small quantity of ether was added. The salt separated slowly in the form of large colorless hexagonal prisms.

0.0987, 0.1207 g. subs. gave 0.0204 and 0.0250 g.  $K_2SO_4$ .

Calc. for  $C_{21}H_{19}O_6K$ : K, 9.60%. Found: K, 9.26, 9.28.

The substance is very soluble in water and in alcohol. Its aqueous solution is neutral to litmus.

**Ethyl-1-phenyl-2-anisoyl Trimethylene Dicarboxate Acid (3-3)** may be prepared by acidifying an aqueous solution of the corresponding potassium salt. The reaction is quantitative. The substance separates in the form of an oil which solidifies on standing, but which is most conveniently extracted with ether. The ester-acid separates from the dry ethereal solution on evaporation, or on the addition of a small quantity of ligroin in the form of large, colorless hexagonal prisms.

0.1449 and 0.1556 g. subs. gave 0.3622 and 0.3882 g.  $CO_2$ ; and 0.0737, 0.0786 g.  $H_2O$ .

Calc. for  $C_{21}H_{18}O_6$ : C, 68.4%; H, 5.4%. Found: C, 68.1, 68.0; H, 5.6, 5.6.

The substance is very soluble in chloroform, quite soluble in ether and insoluble in ligroin. Its basicity was determined by titration. When hydrolyzed in the presence of an excess of potassium hydroxide it passes into a dipotassium salt, which on acidification gives a dibasic acid melting at  $192^{\circ}$  and identified as 1-phenyl-2-anisoyl-trimethylene dicarmonic acid (3-3).

<sup>1</sup> *Am. Chem. J.*, 49, 178 (1913).

When the ester melting at  $86^{\circ}$  was treated with alcoholates it formed a metallic derivative which on acidification gave an isomeric ester melting at  $82^{\circ}$ . This on further action of the same reagents gave a third isomer melting at  $112^{\circ}$ .

**Methyl  $\beta$ -Benzal- $\beta$ -Anisoyl-methylmalonate** (II and III, p. 1520), M. p.  $82^{\circ}$  and  $112^{\circ}$ .—The labile form of this ester, melting at  $82^{\circ}$ , was prepared by adding a few drops of sodium methylate to a well cooled ethereal solution of the ester melting at  $86^{\circ}$ . The separation of a solid metallic derivative took place slowly. This consisted of fine, yellow needles which were filtered and washed with ether. It was decomposed by shaking with ether and cooled hydrochloric acid; and the colorless ethereal solution, after being washed free from acid and dried over calcium chloride, gave an almost pure product melting at  $82^{\circ}$ . The yield varied between 30 and 50%. This was improved by modifying the method, magnesium methylate being substituted for sodium methylate, when a yield varying between 70 and 90% was obtained. The procedure in this case was as follows: 1.3 grams of magnesium were dissolved in 27 cc. of methyl alcohol to which a small quantity of mercuric chloride had been added. At the conclusion of this reaction, 10 g. of the ester melting at  $86^{\circ}$  were added to the mixture in small quantities, and in the form of a fine powder; and its solution took place immediately. The solution was heated on the water bath for about an hour, part of the alcohol was then distilled off, and the residue shaken with ether and cooled hydrochloric acid. The ethereal solution after being washed free from acid and dried over calcium chloride, deposited a crystalline solid melting at  $82^{\circ}$ . This substance was finally purified by recrystallization from ether and alcohol.

0.1373 and 0.1671 g. subs. gave 0.3486 and 0.4249 g.  $\text{CO}_2$ ; and 0.0629, 0.0755 g.  $\text{H}_2\text{O}$ .  
Calc. for  $\text{C}_{21}\text{H}_{20}\text{O}_6$ : C, 68.4; H, 5.4. Found: C, 69.2, 69.3; H, 5.0, 5.0.

The substance is extremely soluble in ether and in hot methyl alcohol. It crystallizes from both solvents in the form of long, fine needles, which appear soft and felt-like while moist, but which dry in hard lumps. It readily reduces potassium permanganate in solution in acetone. In solution in chloroform or carbon tetrachloride, the substance reacts readily with a molecular equivalent of bromine. The reaction was attended by the evolution of hydrobromic acid, but the resulting oil showed no tendency to form a solid product. When the ester in solution in methyl alcohol was treated with an equivalent of potassium hydroxide dissolved in the same solvent, the separation of a deeply colored metallic derivative took place at once. The substance crystallized in the form of coarse, orange-colored needles, which were filtered, washed with alcohol, and analyzed.

0.0730, 0.0831 and 0.0904 g. subs. gave 0.0149, 0.0170 and 0.0185 g.  $K_2SO_4$ .  
Calc. for  $C_{21}H_{19}O_6K$ : K, 9.6%. Found: K, 9.15, 9.17, 9.17.

The substance is insoluble in water and ether, but dissolves readily in alcohol forming deep red solutions. The solution in alcohol is very unstable, and the color was completely discharged upon standing, or upon boiling the solutions. When the dry metallic derivative was shaken with ether and hydrochloric acid, it passed back quantitatively into the ester, melting at  $82^\circ$ .

The stable form of  $\beta$ -benzal- $\beta$ -anisoyl-methylmalonate, m. p.  $112^\circ$ , was formed by the action of sunlight on an ethereal solution of the low melting ester, in the presence of a small quantity of iodine. The transformation was quantitative. The same substance was obtained by treating the ester, m. p.  $82^\circ$ , with sodium and magnesium methylates and decomposing the product with hydrochloric acid. Since the yield was better in the case of the latter reagent, the procedure in this case will be described. Magnesium methylate was prepared by dissolving 1.3 g. magnesium in 27 cc. methyl alcohol. As soon as the reaction was complete, 10 g. of ester were added to the solution in the form of a fine powder. Either of the isomeric substances, melting at  $86$  and  $82^\circ$  could be used for this reaction. The substance dissolved on warming, and the resulting mixture was evaporated to dryness on a water bath. If the dried residue appeared greenish or yellow, a small quantity of alcohol was added and the mass was again evaporated to dryness. This process was repeated until the product appeared white. The mass was then decomposed by shaking with ether and cooled hydrochloric acid, when the final product, which is sparingly soluble in ether, separated in crystalline form. It was filtered, washed with ether and dried. It was further purified by recrystallizing from chloroform-ether mixtures. The yield varied between 80 and 90%.

0.1628, 0.1701 and 0.1547 g. subs. gave 0.4100, 0.4293, 0.3913 g.  $CO_2$ , and 0.0743, 0.0747, 0.0683 g.  $H_2O$ .

Calc. for  $C_{21}H_{19}O_6$ : C, 68.4%; H, 5.4%. Found: C, 68.7, 68.8, 68.9; H, 5.1, 4.9, 4.9.

The substance is very soluble in chloroform, soluble in hot alcohol, sparingly soluble in cold alcohol, and almost insoluble in ether. It separates from chloroform-ether mixtures, or from solutions in hot alcohol, in the form of large, well-defined prisms. Dissolved in chloroform or carbon tetrachloride, it readily reacts with an equivalent of bromine. The reaction was attended by an evolution of hydrobromic acid, but the resulting oil gave no solid product. A solution of the substance in acetone immediately reduced permanganate in solution in the same solvent. Subjected to prolonged heating with magnesium methylate, it suffered no change and was regenerated quantitatively when shaken with ether

and hydrochloric acid. When the ester in solution in methyl alcohol was treated with potassium hydroxide dissolved in the same solvent, a highly colored metallic derivative was formed. This substance separated immediately in the form of long, fine, yellow needles, which were soft and felt-like while moist. It was filtered, washed with ether, and analyzed.

0.0991, 0.1173, 0.1420 g. subs. gave 0.0196, 0.0232 and 0.0280 g.  $K_2SO_4$ .

Calc. for  $C_{21}H_{19}O_6K$ : K, 9.6%. Found: K, 8.87, 8.87, 8.84.

The substance is insoluble in water and in ether, but is very soluble in alcohol. Like its isomer it is very unstable in solution, the deep red color of its alcoholic solutions being quickly discharged even upon standing in the cold. The dried substance, when shaken with ether and hydrochloric acid, passed back quantitatively into the ester, melting at  $112^\circ$ .

When the esters melting at  $82$  and  $112^\circ$ , in solution in alcohol, are hydrolyzed by concentrated aqueous potassium hydroxide, the metallic derivative which at first forms, dissolves on standing or upon boiling. The resulting straw-colored liquid was poured into water in a separatory funnel, and extracted repeatedly with ether. The ether when washed, dried and evaporated, left no residue, showing the absence of any neutral product, and showing also that the original ester had been completely hydrolyzed. The alkaline solution when acidified precipitated a yellow oil. This was found to consist of a mixture of acids, three of which were finally separated and identified. They were 1-phenyl-2-anisoyl-trimethylene dicarbonic acid (3-3), m. p.  $192^\circ$ ;  $\beta$ -anisoyl-propionic acid, m. p.  $147^\circ$ ; and  $\beta$ -benzal- $\beta$ -anisoyl-propionic acid, m. p.  $124^\circ$ . The first was found to be identical with the dibasic acid obtained by the hydrolysis of the ester melting at  $86^\circ$ . The second and third were acids whose identity was established by syntheses to be described later in this paper.

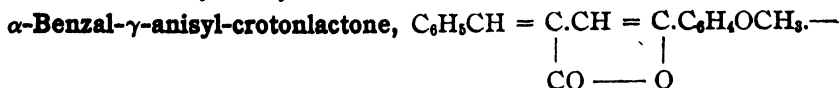
Both the dibasic acid and the ester-acid, obtained by hydrolyzing the ester, m. p.  $86^\circ$ , lose carbon dioxide when heated at about  $200^\circ$ . The result of the decomposition of the first named substance was a mixture from which four solid products were isolated.

When the acid, melting at  $192^\circ$ , was heated at about  $210^\circ$ , it was decomposed with an evolution of carbon dioxide. At the same time it changed color first to amber and then to greenish brown. When gas was no longer evolved, the product was poured at once into a small quantity of alcohol-free ether. The mixture dissolved at once in the ether, but in the course of a few moments the separation of a greenish brown precipitate took place. The precipitate consisted of a mixture of three substances, all of which are very sparingly soluble in ether. The pre-

precipitate was filtered, washed with ether and the products separated by fractional crystallization from ethyl acetate. They consisted of a yellow and a green unsaturated lactone, melting at about 173 and 176°, respectively; and of a monobasic acid melting at 198°. After the separation of these substances, the filtrates contained in ethyl acetate and ether were combined, and the mixture was then extracted repeatedly with dilute sodium carbonate in order to remove the acid products. The ethereal solution containing neutral substances was then washed, dried and allowed to evaporate. It gave an oil from which small quantities of the yellow lactone slowly crystallized. No other solid product was separated. Since this oil represented at least 80% of the original dibasic acid, the attempt was made to study it by dissolving it in sodium methylate and then acidifying. The oil was readily soluble in this reagent, and the solution on dilution with water remained clear. The addition of hydrochloric acid to the aqueous solution caused the precipitation of a yellow oil which was found to consist in large part of  $\beta$ -anisoyl-propionic acid. The identification was made by comparison with a specimen of this acid obtained by synthesis.

The sodium carbonate extracts were combined and extracted once with ether. Either of two subsequent methods of procedure were employed—favoring, respectively, the separation of one or the other of two monobasic acids whose sodium salts were present in the alkaline solution. (a) The aqueous solution containing sodium carbonate was acidified with hydrochloric acid. A yellow oil was precipitated which partially solidified on standing. The acid solution was decanted, the oil was washed with water and allowed to stand until it seemed quite dry. The addition of a small quantity of alcohol-free ether caused the immediate separation in crystalline form of additional small quantities of the acid melting at 198°. It was necessary to handle the material very quickly at this point, and to filter the acid at once; since, upon standing, it passed into solution in ether, the ethereal solution on evaporation giving an oil which showed no tendency to crystallize. (b) The aqueous solution containing sodium carbonate was evaporated to dryness on a water bath, and the residue was extracted repeatedly with small quantities of alcohol in order to remove any soluble salts of organic acids. The alcoholic extracts were then combined, concentrated by evaporation on a water bath, and, when cool, treated with a small quantity of ether. The addition of ether caused the immediate precipitation of a white crystalline substance, and further small additions of ether increased the quantity of this substance. It was filtered, washed with a small amount of acetone, and recrystallized from alcohol or from alcohol-ether mixtures. It was found to consist of a salt, melting at 212°, and its aqueous solution, on addition of hydrochloric acid, gave an unsaturated monobasic acid melting at 124°. The

filtrates from this salt were combined, concentrated on a water bath, diluted with water and acidified. The precipitated oil was taken up with ether, the ether washed, dried, and evaporated. It deposited an oil which showed no tendency to crystallize.



Two substances corresponding to this formula were formed when 1-phenyl-2-anisoyl-trimethylene-dicarboxylic acid (3-3) was heated above 200°. In a series of five parallel experiments, using 20 g. portions of the same specimen of dibasic acid, and varying the temperature between 210 and 250°, it was found that the quantity of colored lactone obtained remained almost constant and corresponded to about 4% of the acid used in the experiment. Quick heating at 230° gave the best yield of solid product when poured into ether, and, therefore, the best yield of the acid melting at 198°. The lactones were readily separated from the acid product by recrystallizing from ethyl acetate. Both substances were prepared by synthesis by methods analogous to those used by Borsche in preparing 1-benzal-3-phenyl-croton-lactone.<sup>1</sup> 18.6 g. of pure sodium  $\beta$ -anisoyl-propionate and 12 g. of benzaldehyde were heated with 24 g. of acetic anhydride in a metal bath at a temperature between 110 and 115° for 24 hrs. The mixture while still hot was treated with 200 cc. of alcohol, allowed to cool, and then filtered, and washed with alcohol. After crystallization from ethyl acetate it gave 5.2 g. of green lactone, m. p. 168-170°. In recrystallizing this, the filtrates yielded the yellow modification. Other products separated from the mother liquors were sodium  $\beta$ -anisoyl-propionate, 7.8 g., and free  $\beta$ -anisoyl-propionic acid, 3.8 g. The reaction thus took place entirely in one sense, although only about one-third of the original salt reacted with benzaldehyde. The lactones obtained in this way were identical in every respect with those obtained by heating the dibasic acid. The relation existing between the green and yellow lactone is very interesting, the results of analysis showing them to be isomeric substances.

0.1012 and 0.1392 g. subs. (yellow) gave 0.2865, 0.3944 g. CO<sub>2</sub>; and 0.0459, 0.0621 g. H<sub>2</sub>O.

0.1261 g. subs. (green) gave 0.3583 g. CO<sub>2</sub> and 0.0589 g. H<sub>2</sub>O.

Calc. for C<sub>18</sub>H<sub>14</sub>O<sub>3</sub>: C, 77.6%; H, 5.0%. Found: C, 77.2, 77.2, 77.4; H, 5.0, 4.9, 5.1.

Both substances melt to a deep red liquid, both dissolve in chloroform and ethyl acetate to give deep red solutions, in acetone alcohol and ether to give yellow or pale greenish yellow solutions. One gram of substance dissolves in 38 g. of ethyl acetate, 66 g. acetone, 14 g. chloroform, and 500

<sup>1</sup> Ber., 47, 1114 (1914).



g. ether, respectively. In recrystallizing from all solvents about one-third of the green lactone passes over into the yellow modification. Both substances crystallize from all solvents in the form of long, glistening plates. In the matter of chemical properties the only point of difference observed was that the green modification instantly reduced permanganate in solution in acetone, while the yellow form did not. Both dissolve in alcoholic potassium hydroxide, and sodium methylate; and these solutions, when diluted with water and acidified, gave the same acid. This acid, when recrystallized from chloroform-ligroin mixtures, melted at  $165^{\circ}$ . It corresponds to  $\alpha$  phenylacetyl-cinnamic acid, obtained in an analogous manner by Borsche.

**$\alpha$ -Benzal- $\beta$ -anisoyl-propionic Acid,**  $C_6H_5CH = C.CH_2COC_6H_4OCH_3$ ,  

|  
COOH

was obtained from the corresponding crotonlactone in the manner described. It separated from aqueous alkaline solutions as a fine, white flocculent precipitate on the addition of acid. This was filtered, washed with water and dried. It was recrystallized first from chloroform-ligroin mixtures, and then from acetone from which it separated in long, hexagonal prisms.

0.1099 g. subs. gave 0.2938 g.  $\text{CO}_2$  and 0.0523 g.  $\text{H}_2\text{O}$ .

Calc. for  $C_{18}H_{16}O_4$ : C, 72.9; H, 5.4. Found: C, 72.9; H, 5.3.

The substance is sparingly soluble in water. Its aqueous solution reacts acid toward litmus and reduces permanganate instantly in the cold. The acid dissolves readily in chloroform, ethyl acetate, acetone, and ether, but is almost insoluble in ligroin. In solution in carbon bisulfide it readily decolorizes bromine with the evolution of hydrobromic acid. Its solution in methyl alcohol, when saturated with hydrogen chloride, gives an immediate precipitation of the corresponding yellow crotonlactone, m. p. 173°.

**$\beta$ -Benzal- $\beta$ -anisoyl-propionic Acid**,  $\text{C}_6\text{H}_5\text{CH} = \text{C}.\text{COC}_6\text{H}_4\text{OCH}_3$ .—This

$$\begin{array}{c} | \\ \text{CH}_2\text{COOH} \end{array}$$

acid, m. p. 124°, was formed together with an isomeric acid, m. p. 198°, when 1-phenyl-2-anisoyl-trimethylene dicarbonic acid (3-3) was heated at above 200°. It was separated from the other substances formed as a result of this reaction by means of its sodium salt and in the manner already described. The substance was also prepared by synthesis. The method used was analogous to that employed by Borsche in the preparation of benzoyl-phenyl-isocrotonic acid<sup>1</sup> ( $\beta$ -benzal- $\beta$ -benzoyl-propionic acid). 1.47 g. of sodium in 30 cc. absolute alcohol were cooled with ice-water, and added drop by drop, with constant shaking, to a mixture of

<sup>1</sup> *Ber.*, 47, 1112 (1914).

15 g. of ethyl  $\beta$ -anisoyl-propionate and benzaldehyde. There was no heat evolved during this reaction so far as could be observed. The mixture was allowed to stand overnight and in the morning showed the separation of a solid substance in the form of a white, flaky precipitate. This was filtered and washed, first with alcohol, and then with acetone. When dry it dissolved in water to give a clear solution and this on addition of hydrochloric acid gave an oily precipitate. This, when washed, dried, and recrystallized, gave an acid melting at  $124^{\circ}$ . This acid was the only substance that was separated in pure form as a result of this condensation. This yield was, however, very unsatisfactory, since only about 25% of solid product was obtained, the remaining 75% being accounted for as an oil which showed no tendency to crystallize. The acid was purified by crystallization from chloroform-ligroin mixtures and then from acetone from which it separated in long, hexagonal prisms.

0.1496 and 0.1694 g. subs. gave 0.3951, 0.4475 g.  $\text{CO}_2$ ; and 0.0704, 0.0803 g.  $\text{H}_2\text{O}$ .  
Calc. for  $\text{C}_{18}\text{H}_{16}\text{O}_4$ : C, 72.9%; H, 5.4%. Found: C, 72.0, 72.0; H, 5.2, 5.2.

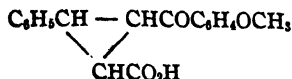
The substance is soluble in ether, chloroform, ethyl acetate and acetone, 1 g. of substance dissolving in 15, 8, 6 and 2.4 g. of these solvents, respectively. It is insoluble in ligroin and only slightly soluble in hot water, from which it crystallizes on cooling. Its aqueous solution gives an acid reaction with litmus and reduces permanganate instantly in the cold. When dissolved in methyl alcohol saturated with hydrogen chloride, it passes into an oil. This oil showed no tendency to crystallize after standing for months.

**Sodium  $\beta$ -Benzal- $\beta$ -anisoyl-propionate** was obtained when phenyl-anisoyl-trimethylene dicarbonic acid was decomposed and the product treated in the manner described. It was purified by repeated recrystallizations from alcohol, and from alcohol-ether mixtures, from which it separated in the form of soft, white needles melting at  $212^{\circ}$ .

0.1805 and 0.1515 g. subs. gave 0.0368 and 0.0307 g.  $\text{Na}_2\text{SO}_4$ .  
Calc. for  $\text{C}_{18}\text{H}_{16}\text{O}_4\text{Na}$ : Na, 7.32%. Found: Na, 6.60, 6.56.

The salt is very soluble in water and in hot alcohol, less soluble in cold alcohol, and insoluble in ether. Its aqueous solution when acidified with hydrochloric acid deposited a white oil, which crystallized on standing and which consisted of pure  $\beta$ -benzal- $\beta$ -anisoyl-propionic acid. An aqueous solution of the salt reduced permanganate as rapidly as added. The reaction was accompanied by the liberation of benzaldehyde which was recognized by its odor. The products of the reaction were readily separated and identified as benzoic and anisic acids.

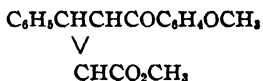
**1-Phenyl-2-anisoyl-trimethylene-3-monocarbonic Acid,**



This acid was obtained in very small quantities along with  $\beta$ -benzal- $\beta$ -anisoyl-propionic acid\* as a result of heating the dibasic acid. It was separated as one of a number of substances formed when methyl  $\gamma$ -bromo- $\gamma$ -anisoyl- $\beta$ -phenyl-butyrate<sup>1</sup> was heated with dimethyl aniline. It was obtained in the form of its methyl ester when the ester acid, m. p.  $162^\circ$ , was heated above  $200^\circ$ . The acid was purified by recrystallizing from acetone and ethyl acetate and washing with ether. It crystallized from acetone in the form of prisms, m. p.  $198^\circ$ .

0.1207 and 0.1108 g. subs. gave 0.3230 and 0.2958 g.  $\text{CO}_2$ ; and 0.0576, 0.0529 g.  $\text{H}_2\text{O}$ .  
Calc. for  $\text{C}_{18}\text{H}_{16}\text{O}_4$ : C, 72.9%; H, 5.4%. Found: C, 72.9, 72.8; H, 5.3, 5.3.

The substance is sparingly soluble in ether, chloroform, ethyl acetate and acetone, 1 g. of substance dissolving in 514, 87, 35 and 15 g. of these solvents, respectively. It is slightly soluble in water, its aqueous solution giving an acid reaction with litmus. In solution in carbon tetrachloride it decolorized bromine with the evolution of hydrobromic acid. Its solution in methyl alcohol saturated with hydrogen chloride deposited a crystalline ester on standing.



was formed from the corresponding acid in the method just described. It was also obtained as a result of heating the ester-acid, m. p.  $162^\circ$ , at about  $200^\circ$ . It was purified by ether-ligroin mixtures, and finally by recrystallizing from methyl alcohol.

0.1364 and 0.1260 g. subs. gave 0.3657, 0.3382 g.  $\text{CO}_2$  and 0.0678, 0.0624 g.  $\text{H}_2\text{O}$ .  
Calc. for  $\text{C}_{18}\text{H}_{16}\text{O}_4$ : C, 73.5%; H, 5.8%. Found: C, 73.1, 73.2; H, 5.5, 5.5.

The substance is very soluble in ether and in hot methyl alcohol, less soluble in cold alcohol, and sparingly soluble in ligroin. It crystallizes in the form of soft, white, glistening needles, melting at  $121^\circ$ . When dissolved in alcoholic potassium hydroxide and poured into water the solution remained clear, but on acidifying with hydrochloric acid, precipitated an oil which partially solidified upon standing. The solution was decanted, the oil was washed and allowed to stand until it appeared quite dry. The addition of a small quantity of ether caused the separation of a white crystalline solid, which was filtered at once and washed with ether. It consisted of the acid, m. p.  $198^\circ$ .

**$\beta$ -Anisoyl-propionic Acid**,  $\text{CH}_3\text{OC}_6\text{H}_4\text{CO}\cdot\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$ , was obtained as one of the decomposition products formed when the unsaturated methyl esters melted at  $82^\circ$  and  $112^\circ$ , respectively, were hydrolyzed in the presence of an excess of aqueous potassium hydroxide. It was also obtained from residues that had stood for some time after the separation of the main products formed by heating the dibasic acid. It was prepared

<sup>1</sup> *Am. Chem. J.*, 49, 177 (1913).

synthetically by a method analogous to that used by Borsche in the preparation of  $\beta$ -benzoyl-propionic acid.<sup>1</sup> One part anisole was added to 1 part succinic anhydride and 1.5 parts  $\text{AlCl}_3$  suspended in 4 parts carbon disulfide. The mixture was heated on a water bath until hydrogen chloride was no longer evolved. The dark red semisolid addition product was decomposed with ice, when a white, insoluble product was obtained. The crude product was dried, and was finally purified by preparing ethyl- $\beta$ -anisoyl propionate, recrystallizing it, and from it, regenerating the acid. This was then further purified by recrystallizing from acetone, from which it separated in large hexagonal prisms, m. p.  $147^\circ$ .

0.1354 and 0.1318 g. subs. gave 0.3141, 0.3058 g.  $\text{CO}_2$ ; and 0.0623, 0.0614 g.  $\text{H}_2\text{O}$ ; (recrys.) 0.1344 g. gave 0.3136 g.  $\text{CO}_2$  and 0.0663 g.  $\text{H}_2\text{O}$ .

Calc. for  $\text{C}_{11}\text{H}_{12}\text{O}_4$ : C, 63.4%; H, 5.7%. Found: C, 63.2, 63.2, 63.6; H, 5.1, 5.1, 5.4.

The acid is sparingly soluble in most organic solvents, one part dissolving in 54 parts acetone, 48 parts ether, 36 parts ethyl acetate and 30 parts methyl alcohol. It is soluble in hot water, 15 parts of substance dissolving in 800 parts of solvent, from which about 90% crystallizes on cooling. Its solutions in methyl and ethyl alcohol, when saturated with hydrogen chloride, gave the corresponding esters. These melted at  $47^\circ$  and  $52^\circ$ , respectively. Both are very soluble in alcohol and ether, but may be readily purified by recrystallization from their respective alcohols, from which they crystallize in large colorless crystals. The acid contains hydrogen that is exceedingly sensitive to oxidizing agents, and its sodium salt reduces permanganate solution instantly in the cold. The products of this oxidation were anisic acid, and another acid product which was not fully studied. It was very soluble in water, from which, however, it was readily extracted by ether. The dried ethereal solution on evaporation deposited the acid in the form of large, glistening, white plates, but the substance was so extremely sensitive that its solution in ligroin decomposed with the deposition of carbon when evaporated on the water bath.

MT. HOLYOKE COLLEGE LABORATORY.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF SOUTH DAKOTA.]

## THE MONONITRO PHENYL ETHERS.

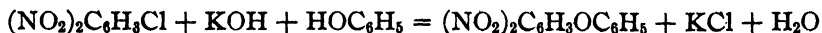
BY HILTON IRA JONES AND ALFRED N. COOK.

Received April 25, 1916.

In 1873 Maikopar<sup>2</sup> made a dinitrophenyl ether by heating dinitrochlorobenzene, caustic potash and phenol in alcoholic solution. These substances react according to the following equation:

<sup>1</sup> *Ber.*, 47, 1110 (1914).

<sup>2</sup> *Ibid.*, 6, 564 (1873).



Maikopar seems to have been the first chemist to use this general method, which has been brought into prominence by the work of Willgerodt, Haeussermann, Ullmann and Cook.

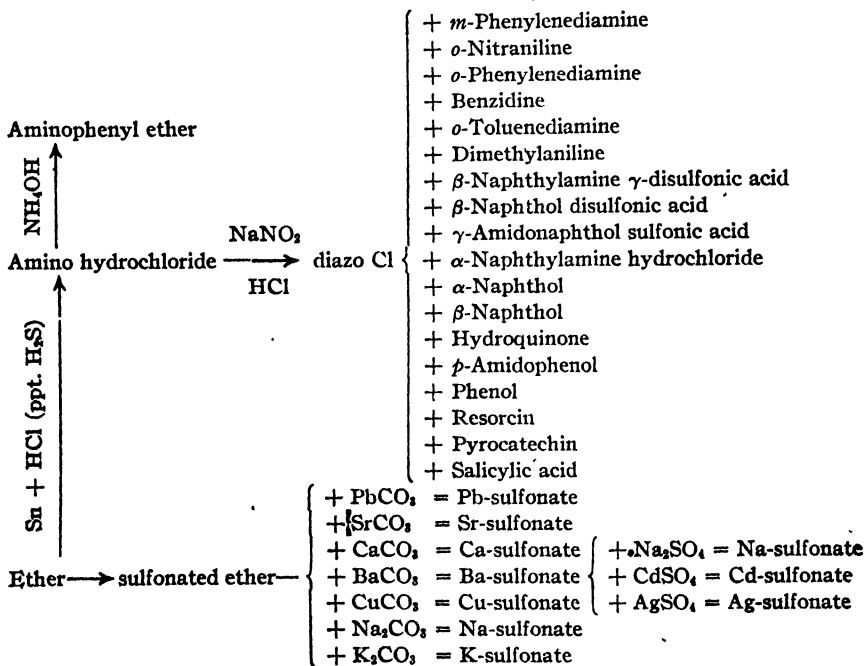
The presence of the negative nitro group makes it much easier to manufacture the nitrophenyl ethers than the corresponding non-nitro compounds. An increasing number of negative groups seems to enhance this effect. Thus picryl chloride and potassium phenolate give a much better yield than the phenolate with either *o*- or *p*-bromonitro benzene. The position of the nitro group in reference to the halogen also has a marked effect both on the stability of the substance and the yield as well as the ease of production. Thus, following the usual rule, a *m*-bromonitro benzene will scarcely react with potassium phenolate at all unless a catalytic agent be present, and the ortho compound reacts more easily than the para, the reaction going to completeness on the boiling water bath in case of the ortho compound, while it requires a temperature of 135 to 140° for the para. The yield of ether produced is greater in case of the ortho, though if it is freed from the other reaction products by distillation, it is liable to be less because of its greater instability and consequent decomposition at a higher temperature. Performed in this way we have obtained from the para compound 81% of the theoretical yield of ether, and from the ortho compound 67%. But if, instead of separating by distillation, the reaction compound is extracted with ether, sulfonated and converted into the potassium salt, the yield in case of the ortho compound was 85% of the theory, while the yield in case of the para compound was 82%. The para compound reduces much more easily than the ortho. It is sometimes very difficult to isolate these in pure form. These amino compounds in turn may be diazotized and converted into a large number of dyes, or the amino ethers may be coupled with other diazonium compounds with similar results. The ortho amino and diazonium compounds are much more unstable than the corresponding para compounds. The ortho aminophenyl ethers yield the more brilliant shades as well as the widest variety of colors. The shades of the sulfonated dyes seem somewhat less brilliant than the unsulfonated. The ortho nitrophenyl ethers are readily converted into the sulfonic acids by treatment with concentrated sulfuric acid in the cold. The para compounds sulfonate with greater difficulty, treatment with sulfuric acid on the boiling water bath being necessary. The para compounds are uniformly better crystalline than the ortho, less soluble and without exception melt and distil at higher temperatures. The *p*-nitrophenyl ether is beautifully crystalline and readily sublimes, while all efforts to reduce the *o*-nitrophenyl ether to a crystalline state by cooling far below zero have failed.

## Experimental Part.

TABLE I.

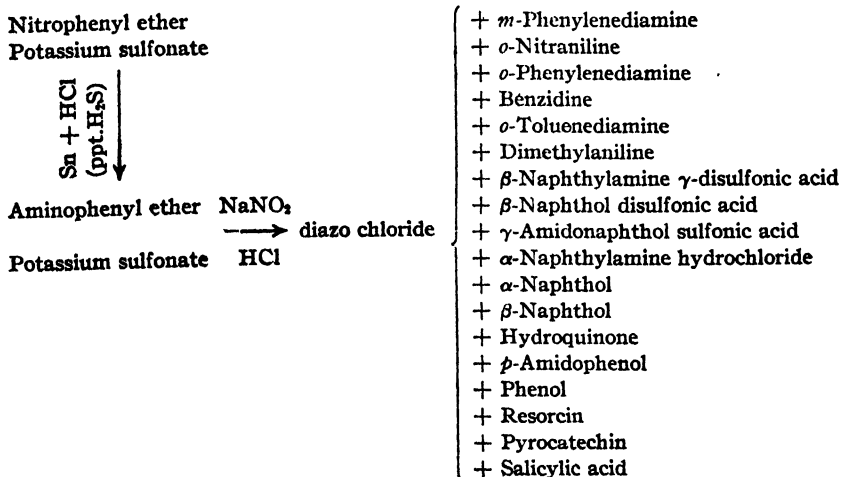
## General Outline.

## I. The Unsulphonated Dyes.



## General Outline.

## II. The Sulfonated Dyes.



**Potassium Phenolate.**—In the earlier experiments of Maikopar<sup>1</sup> and Willgerodt,<sup>2</sup> an alcoholic solution of potassium hydroxide and phenol was employed. In one of his experiments he also used carbon bisulfide as a solvent. Haeussermann and Teichmann<sup>3</sup> were the first to use potassium phenolate with phenol as a menstruum. They made the potassium phenolate by treating phenol with metallic potassium in an atmosphere of hydrogen. For use in preparing various phenyl ethers, Cook<sup>4</sup> made potassium phenolate by dissolving both phenol and alkali in a small amount of water, evaporating to dryness on a water bath and heating to 100° in an air bath. In later experiments he made the potassium phenolate without the use of any water and showed<sup>5</sup> that better yields are obtained by using the phenolate made with KOH and phenol. Our recent work confirms this conclusion. We have found the most convenient way of preparing potassium phenolate is to take 50 g. of phenol and 35 g. of potassium hydroxide, purified by alcohol, and melt each separately with the smallest possible amount of heat. The molten hydroxide is then poured with active stirring into the molten phenol and the product heated on a low flame with constant stirring until it just begins to form a hard ball on the rod. It is removed and placed in a flask and tightly corked. It is best to powder it while hot. This method gives a snow-white product free from the objectionable charring which usually occurs. This method is applicable to the preparation of various phenolates except when they contain one or more nitro groups, in which case they ignite spontaneously.

***o*-Nitrophenyl Ether.**—13.2 grams of potassium phenolate prepared as above are mixed with 20.2 g. of powdered *o*-bromonitro benzene, being one-tenth gram molecule of each, heated for two hours on a boiling water bath until the reaction compound is of a homogeneous reddish brown color and granular appearance. All the earlier workers in making the phenyl ethers by this method thought it necessary to use some substance as a menstruum—alcohol, carbon bisulfide or phenol. We now know that the use of any menstruum is in some cases unnecessary and in others harmful. The reaction product is not extracted with ether as was done by the early experiments, but distilled directly *in vacuo*. On redistillation the pure *o*-nitrophenyl ether is obtained, boiling at 195 to 197° under 45 mm. pressure<sup>6</sup> with partial decomposition. It boils without decomposition at 13 mm. pressure. A sample was seven times distilled and reduced to a temperature of —80° with solid carbon dioxide and ether. Under these

<sup>1</sup> *Ber.*, 6, 564 (1873).

<sup>2</sup> *Ibid.*, 12, 762 and 1277 (1879); 13, 887 (1880).

<sup>3</sup> *Ibid.*, 29, 1446 and 2083 (1896); 30, 738 (1897).

<sup>4</sup> *Am. Chem. J.*, 24, 525 (1902).

<sup>5</sup> *THIS JOURNAL*, 25, 60 (1903).

<sup>6</sup> Haeussermann and Teichmann give the boiling point as 205° at 45 mm. and Ullmann 185° at 55 mm.

conditions the liquid became very viscous, but showed no signs of crystallization. Ortho nitrophenyl ether has a pleasing, characteristic, ethereal odor. It is very soluble in alcohol, ether, benzene, xylene, toluene, carbon bisulfide and chloroform. It is but slightly soluble in ligroin and entirely insoluble in water. Its specific gravity at  $21.5^{\circ}$  is 1.2539. The ether shows the peculiar property of not wetting glass, but draws away from it like water from a glass that is oily. The surface tension was found to be 0.6225, as compared with water, and 44.882, absolute. The viscosity was 13.17, as compared with water, and 6.664, absolute, both being determined at  $25^{\circ}$ . The refractive index<sup>1</sup> at  $20^{\circ}$  is 1.575. The ether when freshly distilled is a golden yellow color, but shows signs of darkening on long standing.

**The Free Sulfonic Acid,** ( $\text{NO}_2\text{C}_6\text{H}_4\text{OC}_6\text{H}_4\text{SO}_3\text{H}$ ).—The free sulfonic acid of *o*-nitrophenyl ether was prepared from the corresponding cadmium sulfonate (*q. v.*) by dissolving this salt in hot water, precipitating the cadmium with hydrogen sulfide and removing the water from the solution by distillation *in vacuo*. When the solution had been reduced to very small volume it was removed and placed in an evaporating dish in a vacuum desiccator over sulfuric acid. After a few hours the free sulfonic acid crystallized out in glistening white flakelets which grouped themselves together in radial systems resembling hoar frost. These crystals on exposure to the air soon liquefied, and if exposed to the light, lose their luster and darken. The crystals melt at  $90^{\circ}$  with decomposition. When a water solution of the acid is added to a soda solution, a brisk effervescence results. The free acid is unstable, very hygroscopic and extremely soluble. An analysis was not attempted because of this hygroscopic character.

**The Sulfonic Acid Salts.**—The sulfonic acid salts of *o*-nitrophenyl ether were prepared in two ways. First, the ether was sulfonated by treating with three volumes of concentrated sulfuric acid. This was warmed for thirty minutes on a water bath. The ether turns red during this process and complete solution takes place. As soon as the ether is completely sulfonated the reaction product is poured into a large excess of water. The whole is heated to boiling and completely neutralized with the carbonate of the metal whose salt is sought. The solution was filtered boiling hot and evaporated to crystallization. In a few cases the slight solubility of the salt has made it necessary to treat the solid residue once more with boiling water. The second method of making the salts is to treat the barium sulfonate with equal molecules of the sulfate of the metal whose salt is sought and evaporating to crystallization after filtering.

Nine salts have been prepared by these methods. In every case the

<sup>1</sup> Determined by Professor A. L. Haines.



salts have crystallized in radial systems when pure. In many cases the salts at first have crystallized in thin plates and arranged themselves in the radial form only after repeated crystallization. The solubilities of the salts show wide variation, but appear to follow certain regularities, depending upon their position in the periodic system. The analysis of the salts for the metal gives in every case results which are slightly too high. The results for nitrogen seem to be uniformly too low. If this is actually caused by occlusion, it seems strange that repeated crystallization does not change the percentage. The following tabulation shows how the salts were prepared, their crystal form, solubility and analysis:

TABLE II.

Name of salt.	Method of preparation.	Nature of crystals.	Solubility in 100 cc. at 20° C.	Analysis.	
				Found.	Theory.
Barium.....	Carbonate on sulfonic acid	Thin glistening plates	0.51	Ba	Ba
	Carbonate on sulfonic acid			Sr	Sr
Strontium.....	Carbonate on sulfonic acid	Friable warts	2.46	Ca	Ca
	Carbonate on sulfonic acid			N <sub>2</sub>	N <sub>2</sub>
Calcium.....	acid	Shiny scales	10.578	6.51	6.37
		Glistening white granules		N <sub>2</sub>	N <sub>2</sub>
Sodium.....	Both methods were used	Radial aggregations of thin plates	9.872	4.14	4.40
		Warty masses of thin scales		K	K
Potassium.....	Both methods were used	Thin plates	4.02	11.80	11.73
Copper.....	Decomposition of the barium salt	Large thin glistening plates	44.48	Cu	Cu
	Decomposition of the barium salt			9.85	9.74
Cadmium.....	barium salt	Thin plates which darken in the light	3.64	N <sub>2</sub>	N <sub>2</sub>
		very quickly		1.98	1.91
Silver.....	Decomposition of the barium salt	Hard, brownish warts	1.44	...	Ag
Lead.....	Both methods were used	Hard, brownish warts	8.20	...	25.65
					N <sub>2</sub>
					1.69

All the salts were heated in an air bath first to 108° and then to 125° in an attempt to determine whether the salts contained water of crystallization or not. In only two cases did the loss seem to correspond to definite amounts of water of crystallization. The barium salt contained water equivalent to one-half molecule, and the copper salt an amount equalling exactly two molecules of water. The potassium salt lost no water at all on heating. The copper and the silver salts are both difficult to isolate in pure form, the former because of its extreme solubility, which made final evaporation in a vacuum desiccator necessary, and the latter because of its unusual sensitiveness to light. It was finally prepared in the dark by removing the water *in vacuo*. When so prepared it is of glistening whiteness, but it darkens somewhat even when kept in a deep red bottle. The crystals are slippery to the touch, some-

what like boric acid. The copper, silver, cadmium and lead salts are readily darkened by traces of hydrogen sulfide in the air, the lead salt being unusually sensitive. Practically every one of the salts darkens on exposure to the light and air, the sodium and potassium salts being the least affected.

***o*-Nitrophenyl Ether Sulfonyl Chloride.**—The sulfonyl chloride of nitrophenyl ether was prepared by taking 2 g. of ortho nitrophenyl ether sodium sulfonate, powdering, and thoroughly mixing in a mortar with 4 g. of powdered phosphorus pentachloride. As no action took place at once, it was heated on a steam bath for some minutes when the color became darker and the whole assumed a waxy appearance. The reaction product was then added to ice water in a flask and shaken for some minutes, when the oil that first separated crystallized out. The sulfonyl chloride was separated from the water by filtration with suction. It was in the form of round granules. These are insoluble in water, but soluble in hot alcohol from which they crystallized on standing into beautiful, needle-like, white crystals.

***o*-Aminophenyl Ether Hydrochloride.**—It is not easy to reduce ortho nitrophenyl ether to the corresponding amino compound by the ordinary methods, although if the alcoholic solution is boiled with tin and hydrochloric acid for eight hours, using a reflux, the reduction may be brought about. Complete reduction is determined by complete solution. As soon, therefore, as a few drops of the solution when removed and added to a large volume of water failed to leave behind an insoluble oil, the action was judged to be complete. The ether is best reduced, however, by the stannous chloride method first suggested by Ullmann.<sup>1</sup> By evaporating the menstruum long needle crystals of the tin salt separate out. These are dissolved in water which is slightly acid with hydrochloric acid and the tin completely removed by means of hydrogen sulfide. The filtrate must not be heated in contact with the air for the compound is easily oxidized. The water is therefore distilled off to small volume *in vacuo*. The crystals separate in large scales melting with decomposition at 154°. The free base may be liberated from the hydrochloride by treatment with ammonia. The crude oily mass left when the ether is evaporated is crystallized from xylene, giving crystals that decompose at 43 to 45° and darken on standing.

**The Unsulfonated Diazo Dyes.**—In the preparation of these dyes, the solution of the ortho amino hydrochloride was prepared by boiling the ether with stannous chloride for an hour, or all night with tin and hydrochloric acid as has already been described. After the solution has been de-tinned by hydrogen sulfide, filtered and boiled for some time to remove all traces of the gas, the solution has a distinct and characteristic

<sup>1</sup> *Ber.*, 29, 1878 (1896).

odor resembling that of garlic. A weighed amount of ether having been taken, the solution was made up of such strength that each cubic centimeter contains one-tenth gram of the amino hydrochloride. In like manner the solution of the compound with which the diazotized body is coupled was made of known strength. In this way it was easy to mix correct molecular proportions by measuring the volumes. The *o*-aminophenyl ether hydrochloride solution was cooled with ice to 5° and diazotized with a cold solution of sodium nitrite. Upon evaporation the diazonium salt crystallizes for the most part in round, crystalline balls of reddish brown color. The crystals burn readily but do not explode when heated. Solutions containing equal molecules of the diazotized salt of *o*-aminophenyl ether and the substance to be coupled with it are mixed in the cold and boiled. The dyeing was done upon white nuns-veiling which had been mordanted with dilute tartar emetic solution. The dry dye was obtained in each case and crystallized from alcohol. Most of the dyes decompose when a melting point is attempted. While few of the dyes possess shades which might render them of commercial value in spite of the high cost, the opportunity for comparisons of shade which the preparation of the sulfonated and unsulfonated dyes of both the ortho and para series offers, makes their preparation and study of value. The value of this comparison is increased by the fact that the dye solution in every case is of exactly the same concentration, so that shades are strictly comparable. The abbreviations used in the following table are those employed in the Milton Bradley Color Standard supplied with Mulliken's "Identification of Pure Organic Compounds." It is impossible to give an accurate idea of the exact tone of the color without the dyed samples for comparison, and yet this Color Standard makes at least an approach to this possible. All the dyes of this series have been tested thoroughly for light and wash-fastness and in no case has one of them faded.

**The *o*-Aminophenyl Ether Dyes—Sulfonated Series.**—In the preparation of these dyes *o*-nitrophenyl ether potassium sulfonate was reduced with tin and hydrochloric acid. It is noticed that the introduction of the sulfonic acid radical makes the reduction of the nitro group much easier. The reduction is accomplished in this case within a half hour by using tin and hydrochloric acid and heating over a water bath. It is not possible, however, to determine the point of complete reduction in this case so easily as with the unsulfonated ether because the compounds before and after the reduction are both soluble. When reduction is complete, which is best told by a change of color, the solution is de-tinned and diazotized. The diazotized solution was then coupled with the same eighteen reagents as before and a new series of sulfonated phenyl ether dyes obtained. The shades of the dye on wool as well as those of the dry dyes are shown in Table III. The dye obtained in this case with

TABLE III.

Diazotized <i>o</i> -Aminophenyl Ether Hydrochloride Coupled with:				The Potassium Sulfonate of Diazotized <i>o</i> -Aminophenyl Ether Hydro- chloride Coupled with:			
Name.	Color on wool.	Color on dry dye.	Remarks.	Color on wool.	Color on dry dye.	Remarks.	
<i>m</i> -Phenylene diamine.....	R-ORS <sub>2</sub>	RS <sub>2</sub>	A fine color resembling Bismark brown	ORS <sub>2</sub>	RS <sub>2</sub>	A brilliant tango brown	
<i>o</i> -Nitriline.....	Y-OY	OS <sub>2</sub>	A fast lemon shade	OY	YOT <sub>2</sub>	An intense orange-yellow	
<i>o</i> -Phenylene diamine.....	YOS <sub>2</sub>	Black		OYT <sub>1</sub>	RS <sub>2</sub>		
Benzidine.....	OYS <sub>2</sub>	Black		YT <sub>2</sub>	YO light		
<i>o</i> -Toluene diamine.....	YO medium	Black		OYT <sub>2</sub>	ORT <sub>2</sub>		
Di-nethyl aniline hydro- chloride.....	OY	YOS <sub>1</sub> yellow	An intense, brilliant yellow	VS <sub>1</sub> neut. or alkaline OT <sub>1</sub> acid	VS <sub>2</sub>	The neutral or alkaline dye is an intense and per- manent bluish purple	
$\beta$ -Naphthyl amine $\gamma$ -disul- fonic acid.....	YO	Black		O-YOT <sub>1</sub>	Y light		
$\beta$ -Naphthol disulfonic acid. RO	RO	Black	A tango red	YOT <sub>2</sub>	YOT <sub>1</sub>		
$\gamma$ -Amido naphthol sulfonic acid.....	OR	VRS <sub>2</sub>		OR-ROT <sub>1</sub>	ORT <sub>2</sub>	A soft old rose shade	
$\alpha$ -Naphthyl amine hydro- chloride.....	ORS <sub>1</sub>	RVS <sub>2</sub>		ORS <sub>1</sub>	VRT <sub>2</sub>		
$\alpha$ -Naphthol.....	ROS <sub>1</sub>	BGS <sub>2</sub>		OR-RO	Y light		
$\beta$ -Naphthol.....	RO-OT <sub>1</sub>	Black		OT <sub>1</sub>	Black		
Hydroquinone.....	OYT <sub>2</sub>	Black		OYT <sub>2</sub>	YO dark		
<i>p</i> -Amido phenol.....	R-ORS <sub>2</sub>	Black		OS <sub>2</sub>	Black		
Phenol.....	OYT <sub>2</sub>	Black		OYT <sub>1</sub>	OYT <sub>1</sub>		
Resorcin.....	OS <sub>1</sub>	ROS <sub>2</sub>	A tango yellow	Y	Black	A very pure yellow	
Pyrocatechin.....	OYS <sub>1</sub>	VRS <sub>2</sub>		YT <sub>2</sub>	GBS <sub>2</sub>		
Salicylic acid.....	YO-OYT <sub>2</sub>	YOS <sub>2</sub>		White	R dark		

dimethyl aniline hydrochloride is an unusually pleasing and brilliant bluish purple.

***p*-Nitrophenyl Ether.**—This compound was first made in 1896 by Haeussermann and Teichmann<sup>1</sup> by heating *p*-chloronitro benzene with potassium phenolate dissolved in phenol. It has been more recently made by Mailhe and Murat<sup>2</sup> by the nitration of phenyl ether. We first prepared the compound by the method described by Haeussermann and Teichmann and a very dark reaction product was obtained. On extraction with ether we got a dark-colored extract which on evaporation gave a mass of dark crystals. Recrystallizing once from alcohol, the melting point was 65°. Haeussermann and Teichmann gave 62°, Mailhe and Murat 56°. We next prepared the compound by heating *p*-bromonitrobenzene with potassium phenolate without a solvent for fourteen hours on a boiling water bath. In this process a large amount of sublimate gathered on the walls of the flask. These crystals were white, glistening and of long needle structure. They melted sharply at 123.5°. The reaction product was then distilled *in vacuo* boiling at 209° at 45 mm. The distillate on being recrystallized from alcohol melted at 118°. We questioned if the crystallized sublimate could be *p*-nitrophenyl ether. We, therefore, recrystallized the substance seven times with alcohol, and at last obtained a compound melting sharply at 123°. In our work we have obtained crystals melting all the way from 65° up. It seems certain, therefore, from these facts as well as from the analysis for nitrogen, which showed 12.21%, the theory being 12.3%, that the crystals obtained by sublimation were pure *p*-nitrophenyl ether, and that the true melting point of this compound is 123.5°. There is a marked difference between the stability of *o*- and *p*-nitrophenyl ether. The para compound may be distilled at ordinary pressure with little decomposition, the boiling point being 320°. It is insoluble in water, but slightly soluble in ligroin, but readily soluble in alcohol, ether, chloroform, benzene, acetone and other organic solvents.

***p*-Nitrophenyl Ether Sulfonic Acid.**—The free sulfonic acid of *o*-nitrophenyl ether is prepared with the greatest difficulty by the decomposition of the cadmium salt, while on the other hand, the corresponding acid of the para ether is prepared with the greatest ease. It is much more difficult to sulfonate *p*-nitrophenyl ether, however, fuming sulfuric acid (33%) being required, while concentrated sulfuric acid in the cold sulfonates the ortho ether. To 10 g. of *p*-nitrophenyl ether are added 40 g. of the fuming sulfuric acid. The whole is heated on a water bath for one hour, or until the ether has entirely gone into solution. The reaction product is now poured into 250 cc. of cold water with constant stirring. The free acid crystallizes out at once. It is most conveniently purified by recryst-

<sup>1</sup> *Ber.*, 29, 1446 (1896).

<sup>2</sup> *Compt. rend.*, 145, 715 (1912).

tallizing from hot water. The acid melts at  $132^{\circ}$ , and readily decomposes a soda solution. The crystals do not seem to be at all hygroscopic. An analysis of the acid for sulfur gave 10.79%, the theory being 10.85%.

**The Sulfonic Acid Salts.**—The sulfonic acid salts of *p*-nitrophenyl ether were prepared by neutralizing the acid with the carbonate of the metal, or by decomposing the barium salt with the sulfonate of the metal as in case of the salts of the ortho series. Because of the greater insolubility of the *p*-sulfonic acid and all its salts, a larger volume of water must be used, which should be boiling hot. The filtration by suction must be carried out rapidly and the precipitate thoroughly washed with boiling water. The para salts all have the same radial structure noted in the case of the ortho salts, but the crystals are better formed and larger. The para potassium sulfonate has one of the most beautiful crystal forms we have ever seen, crystallizing in concentric tufts as large as a pigeon's egg, and as delicate as a snow flake. The crystals are of glistening whiteness, and show little tendency to discolor on exposure to light and air. The following table shows the salts prepared, their crystal forms, solubilities, etc.:

TABLE IV.

Name of salt.	Method of preparation.	Nature of crystals.	Solubility in 100 cc. at $20^{\circ}$ C.	Analysis.	
				Found.	Theory.
Barium.....	Carbonate on sulfonic acid	Small, glistening, white flakes	0.25	Ba	Ba
	Carbonate on sulfonic acid	White scales, smaller than Ba	1.312	Sr	Sr
Strontium.....	Carbonate on sulfonic acid	Very delicate radial flakes	3.280	Ca	Ca
	Both methods were used	Brownish, glistening scales	6.694	N <sub>2</sub>	N <sub>2</sub>
Sodium.....	Carbonate on sulfonic acid	Large warts of radial plates	1.902	K	K
	Decomposition of the barium salt	Concentric bluish nodules	10.42	Cu	Cu
Copper.....	Decomposition of the barium salt	Shiny, radial plates	1.713	N <sub>2</sub>	N <sub>2</sub>
	Decomposition of the barium salt	Thin, white flakes which darken quickly	1.221	Ag	Ag
Silver.....	Both methods were used	Brownish nodules	6.29	N <sub>2</sub>	N <sub>2</sub>
				25.65	25.65
Lead.....	Both methods were used	Brownish nodules	6.29	1.69	1.69

***p*-Aminophenyl Ether Hydrochloride.**—*p*-Nitrophenyl ether is much more easily reduced to the amino compound than is the corresponding ortho ether. The ether is dissolved in alcohol and boiled with tin and hydrochloric acid on a water bath for an hour or until an oil is no longer obtained, when a few drops of the substance are transferred to water. The alcohol is now evaporated and if necessary water added to keep the solu-

tion clear. The whole is de-tinned with hydrogen sulfide, filtered and the water evaporated *in vacuo*. When small volume has been reached, the hydrochloride crystallizes out in the distilling flask. The crystals are thin, irregular-shaped plates of glistening whiteness. They are perfectly stable either wet or dry and melt at  $122^{\circ}$ . The salt on analysis gave 16.34% chlorine, the theory being 16.03%.

The hydrochloride in water solution was neutralized with ammonia, which liberated the free amine as an oil. This was extracted with ether and recrystallized from alcohol. It melts at  $95^{\circ}$ . Haeussermann and Teichmann<sup>1</sup> give the melting point as  $84^{\circ}$ . Nollau and Daniels<sup>2</sup> give the melting point as  $33^{\circ}$  to  $34^{\circ}$ . Their product was undoubtedly impure. The body is stable in the air and can be distilled undecomposed. On treatment with chloroplatinic acid the amine gives a chloroplatinate which crystallizes in long reddish brown needles.

**The *p*-Aminophenyl Ether Dyes.**—The amino hydrochloride was diazotized and coupled with various reagents. The same eighteen were used here as in the case of the ortho dyes and in just the same concentration. Nuns-veiling was dyed in each case and samples of the pure, dry dye obtained. The para dyes are much more stable, less soluble and better crystalline than the ortho dyes. Most of them can be obtained in pure form by crystallization in alcohol. Several of these melt sharply and without decomposition. Most of the dyes decompose somewhat, however, as they melt. While the shades obtained with these para dyes are in a few cases not so brilliant as the corresponding ortho dyes, the fact that *p*-nitrophenyl ether is so much more easily and cheaply prepared and also more easily reduced to the amino compound would tend to make them at least commercially of much greater importance. There is also the added fact that the *p*-aminohydrochloride is perfectly stable both when in solution and when dry, whereas the ortho compound must not be heated when exposed to the air. The four dyes made by coupling the diazotized amine with meta phenylene diamine, dimethyl aniline hydrochloride,  $\beta$ -naphthyl amine, gamma disulfonic acid and  $\alpha$ -naphthol, might easily become of commercial importance. Table V is exactly similar to the tables of the ortho dyes. The dye concentration and the color notation are the same as in the preceding tables.

**The *p*-Aminophenyl Ether Dyes — Sulfonated Series.**—*p*-Nitrophenyl ether potassium sulfonate is used as the basis of these dyes. It is reduced with tin and hydrochloric as before and the reduction is accomplished very easily and in short time. The solution of the sulfonated amino hydrochloride, after being de-tinned and filtered, is diazotized with sodium nitrite solution and coupled with the same eighteen reagents as

<sup>1</sup> *Ber.*, 29, 1446 (1906).

<sup>2</sup> *THIS JOURNAL*, 36, 1885 (1914).

TABLE V.  
Diazotized *p*-Amino Phenyl Ether Hydrochloride  
Coupled with:

Name.	Color on wool.	Color of dry dye.	Remarks.	Color on wool.	Color of dry dye.	Remarks.
<i>m</i> -Phenylene diamine.....	OR	RS <sub>2</sub>	From YO to R depend- ing upon concentra- tion	RS <sub>2</sub>	Black	A soft, dark brown
<i>o</i> -Nitraniline.....	YT <sub>1</sub>	Dark gray, neutral		OY	YOS <sub>1</sub>	
<i>o</i> -Phenylene diamine.....	YO	VR		YO	RS <sub>2</sub>	
Benzidine.....	OYS <sub>2</sub>	R dark		OYS <sub>1</sub>	YO dark	
<i>o</i> -Toluene diamine.....	OT <sub>1</sub>	RS <sub>2</sub>		YOT <sub>1</sub>	Black	
	OY alk. VRT <sub>1</sub>			VBS <sub>1</sub> alk. GB acid	GB	A brilliant bluish violet
Di-ethyl aniline hydrochloride acid		VRS <sub>2</sub>			BVS <sub>2</sub>	
$\beta$ -Naphthyl amine $\gamma$ -disul- fonic acid.....	YO	Dark gray, warm	A brilliant tango	YOS <sub>1</sub>	R medium	
$\beta$ -Naphthol disulfonic acid....	ORT <sub>1</sub>	ROS <sub>2</sub>		YT <sub>1</sub>	OS <sub>1</sub>	
$\gamma$ -Amido naphthol sulfonic acid	RT <sub>1</sub>	Black		YOS <sub>1</sub>	R dark	
$\alpha$ -Naphthyl amine hydro- chloride.....	VRS <sub>2</sub>	VBT <sub>2</sub>		ROS <sub>2</sub>	BG medium	A tango brown
$\alpha$ -Naphthol.....	OS <sub>1</sub>	Black		YT <sub>1</sub>	OYT <sub>2</sub>	
$\beta$ -Naphthol.....	YOS <sub>1</sub>	BVT <sub>1</sub>		GYT <sub>1</sub>	GYT <sub>2</sub>	Gray, dark
				GYT <sub>2</sub>	green	
Hydroquinone.....	OYT <sub>1</sub>	Black		GYT <sub>2</sub>	Black	
<i>p</i> -Amido phenol.....	OYS <sub>1</sub>	Black		OYS <sub>2</sub>	YOT <sub>2</sub>	Dyes a light cream
Phenol.....	OYS <sub>2</sub>	Black		Cream		
		Dark gray, warm		YT <sub>2</sub>	Black	
Resorcin.....	YOS <sub>1</sub>	Gray, dark		Cream	Black	Dyes a light cream
Pyrocatechin.....	YS <sub>2</sub>	Gray, dark warm		YOS <sub>1</sub>	RS <sub>2</sub>	
Salicylic acid.....	OYT <sub>2</sub>					



before. The same concentrations are used. The presence of the sulfonic acid group renders the dyes more soluble, less intense and harder to isolate in the crystal form. The para sulfonated dyes differ from the others prepared in being explosive when heated. Indeed many of the sulfonic acid salts of *p*-nitrophenyl ether are very explosive. Table V of sulfonated dyes obtained from *p*-aminophenyl ether is exactly comparable with the other tables and furnishes opportunity for the accurate study of the variation in shade produced by varying the position of the diazonium group and the introduction of the potassium sulfonate group.

### Summary.

1. A new method has been devised for preparing potassium phenolate applicable to all non-nitrophenols.
2. The properties of *o*- and *p*-nitrophenyl ethers have been more fully determined and numerous errors corrected.
3. Eighteen new sulfonic acid salts of *o*- and *p*-nitrophenyl ether have been prepared and studied.
4. Seventy-two diazo dyes have been made and studied. These were equally distributed between the sulfonated and unsulfonated series of both the ortho and para ethers.
5. The effects of the positions of the groups upon the properties of the compounds and the colors of the dyes have been carefully studied and the following points have been observed:
  - a. *o*-Nitrophenyl ether and all its compounds are more soluble than the corresponding para bodies and do not crystallize so well.
  - b. *p*-Nitrophenyl ether and all its derivatives are more stable than the corresponding ortho compounds. This is especially noticeable in the case of the amino hydrochloride and the free sulfonic acid.
  - c. *o*-Nitrophenyl ether is more easily sulfonated, harder to reduce and its amino body is easier to diazotize than the para body.
  - d. The *o*-aminophenyl ether dyes tend mostly to the reds and browns, though a few purple and yellow dyes have been produced.
  - e. The ortho dyes are more brilliant than the para.
  - f. The sulfonated dyes are more soluble and less brilliant than the unsulfonated.

### CHRONOLOGICAL BIBLIOGRAPHY OF THE PHENYL ETHERS.

1. 1845 Ettling and Stenhouse, *Ann.*, 53, 77 and 91.  
First subjected copper benzoate to destructive distillation.
2. 1855 List and Limpricht, *Ann.*, 90, 209.  
Obtained diphenyl ether from the destructive distillation of copper benzoate and called it "phenyl oxide."
3. 1862 Fittig, *Ann.*, 125, 328.  
Obtained diphenyl ether in the same way and separated diphenyl from it by treatment with sulfuric acid.

4. 1866 Lesimple, *Ann.*, 138, 375.  
Obtained a substance which he erroneously considered phenyl oxide by distilling phenyl phosphate with lime.
5. 1870 Clemm, *J. prakt. Chem.*, 1, 161.  
Attempted to prepare trinitrophenyl ether from picryl chloride and sodium phenolate in alcoholic solution, but failed.
6. 1871 Hoffmeister, *Ann.*, 159, 191, and *Ber.*, 3, 747 (24, 123).  
Prepared phenyl ether by treating diazobenzene sulfate with phenol. Carefully studied the compound and settled questions that had been in dispute.
7. 1873 Maikopar (article by Wredon), *Ber.*, 6, 564 (26, 1026).  
First manufactured a nitrophenyl ether by treating a nitro halogen benzene with an alkaline phenolate in alcoholic solution.
8. 1879 Willgerodt, *Ber.*, 12, 762 (36, 716).  
Made a dinitrophenyl ether by using dinitrochlorobenzene and potassium phenolate in carbon bisulfide solution. Probably same compound as in (7).
9. 1879 Willgerodt, *Ber.*, 12, 1277 (36, 923).  
Made a trinitrophenyl ether from picryl chloride using phenol, alcohol and water as a menstruum.
10. 1880 Willgerodt, *Ber.*, 13, 887 (38, 642).  
Made a tetranitrophenyl ether by heating dinitro potassium phenolate and dinitrochlorobenzene in sealed tubes.
11. 1881 Merz and Weith, *Ber.*, 14, 187 (40, 264).  
Prepared phenyl ether by heating phenol with zinc chloride at 350°; yield, 5%; and also by heating phenol with aluminum chloride; yield, 10 to 12%. (See also *Ber.*, 12, 1925.)
12. 1882 Boehmer, *J. prakt. Chem.*, 24, 449; also *Ber.*, 15, 83 (42, 1, 396).  
Made phenol bromophenyl ether by the action of hydrobromic acid on diazophenol nitrate or sulfate.
13. 1882 Niederhaeusern, *Ber.*, 15, 1119 (42, 1, 1211).  
Prepared diphenyl ether by heating sodium phenolate with sodium metaphosphate and obtained methylene diphenyl oxide as a by-product.
14. 1882 Richter, *J. prakt. Chem.*, [2] 23, 349 (42, 1, 618).  
Distilled phenyl phosphate with sodium salicylate and obtained oxydiphenyl ketone which on reduction yielded phenyl ether.
15. 1882 Gladstone and Tribe, *J. Chem. Soc.*, 41, 5.  
Made aluminum phenolate, cresolate and thymolate and distilled these obtaining phenyl ether and some of its derivatives.
16. 1883 Klepl, *J. prakt. Chem.*, [2] 28, 201 (46, 1, 446).  
Prepared *p*-phenoxy benzoic acid by passing carbonic anhydride over *p*-hydroxy benzide. He obtained phenyl ether by distilling *p*-phenoxy benzoic acid with baryta.
17. 1884 Richter, *J. prakt. Chem.*, [2] 23, 293 (46, 1, 324).  
Obtained phenyl ether by distilling phenyl phosphate and sodium salicylate.
18. 1884 Willgerodt and Huetlin, *Ber.*, 17, 1764 (46, 1, 1328).  
Prepared four nitrophenyl ethers by treating di- and trinitrochlorobenzenes with potassium *o*- and *p*-nitrophenolates in alcoholic solution.
19. 1884 Buch, *Ber.*, 17, 2638 (48, 1, 147).  
Made ditolyl ether as a by-product of heating *p*-cresol with zinc chloride.

\* The numbers in parenthesis refer to the location of the abstract in the Abstract Volume of *The Journal of the London Chemical Society*.

20. 1886 Gladstone and Tribe, *J. Chem. Soc.*, **49**, 25.  
Made *m*- and *p*-cresyl ethers by the dry distillation of aluminum cresolates.
21. 1888 Graebe, *Ber.*, **21**, 501 (54, 1, 447).  
Prepared *o*-phenoxy benzoic acid.
22. 1890 Hirsch, *Ber.*, **23**, 3705 (60, 1, 437).  
Decomposed diazobenzene with phenol; yield, 50% of the weight of the aniline used.
23. 1896 Haeussermann and Teichmann, *Ber.*, **29**, 1446 (70, 1, 533).  
Made several nitrophenyl ethers and their derivatives by heating the chloro-nitro benzenes with potassium phenolate and phenol.
24. 1896 Ullmann, *Ber.*, **29**, 1878 (70, 1, 605).  
Makes *o*-nitro- and aminophenyl ethers.
25. 1896 Haeussermann and Bauer, *Ber.*, **29**, 2083 (70, 1, 676).  
Continued the work of Haeussermann and Teichmann using the same methods.
26. 1896 Jeitles, *Monatsh.*, **17**, 65 (70, 1, 434).  
Obtained a diphenyl ether by the distillation of calcium *o*-phenoxy benzoate.
27. 1897 Haeussermann and Bauer, *Ber.*, **30**, 738 (72, 1, 333).  
Continued their former work and prepared numerous compounds.
28. 1898 Peratoner and Ortoleva, *Ital. Gazzetta*, **28**, [1] 197 (74, 1, 643).  
Obtained chlorine derivatives of phenyl ether by treating with sulfonyl chloride.
29. 1900 Cook and Hillyer, *Am. Chem. J.*, **24**, 525 (80, 1, 144).  
Prepared 2-nitro-4'-methylphenyl ether and several derivatives.
30. 1901 Cook and Frary, *Am. Chem. J.*, **28**, 486 (84, 1, 163).  
Prepared 4-nitro-3'-methylphenyl ether and several derivatives.
31. 1901 Haeussermann and Schmidt, *Ber.*, **34**, 376 (82, 1, 126).  
Prepared azoxyphenyl ether by electrolytic reduction of the nitro compound and the corresponding amino compound by using the tin cathode.
32. 1901 Cook, *THIS JOURNAL*, **23**, 806 (82, 1, 92).  
Prepared 2-nitro-2'-methylphenyl ether and 2-nitro-3'-methylphenyl ether and several derivatives.
33. 1902 Cook and Eberly, *THIS JOURNAL*, **24**, 1200 (84, 1, 250).  
Prepared 4-nitro-2'-methylphenyl ether and several derivatives.
34. 1903 Cook, *THIS JOURNAL*, **25**, 60 (84, 1, 337).  
Prepared 4-nitro-4'-methylphenyl ether and several of its derivatives.
35. 1904 Cook, *THIS JOURNAL*, **26**, 302 (86, 1, 400).  
Describes the properties of phenyl ether.
36. 1904 Ullmann, *Ber.*, **37**, 853 (86, 1, 417).  
Made phenoxy benzoic acid using copper as a catalyst.
37. 1905 Ullmann and Sponagel, *Ber.*, **38**, 2311 (88, 1, 644).  
Made phenyl ether using copper as a catalyst and increased the yield from 0.9% to 87%.
38. 1905 Cook, *THIS JOURNAL*, **28**, 608 (90, 1, 495).  
Studied aluminum phenolate and its use in the preparation of phenyl ether.
39. 1905 Reverdin and Dressel, *Ber.*, **38**, 1593 (88, 1, 51).  
Prepared some new nitrophenyl ethers.
40. 1905 Kipper, *Ber.*, **38**, 2490 (88, 1, 648).  
A study of the Friedel and Crafts reaction on phenyl ether.
41. 1906 Cook, *Am. Chem. J.*, **36**, 543 (92, 1, 126).  
The distillation of aluminum *m*-cresolate; the preparation of *m*-tolyl ether and its derivatives.

42. 1906 Ullmann and Sponagel, *Ann.*, **350**, 84 (92, 1, 38).  
A study of the yields obtained with various halogen benzene and alkaline phenolates in the presence of finely divided copper.
43. 1906 Ullmann and Stein, *Ber.*, **39**, 622 (90, 1, 258).  
Made various methoxy and hydroxy phenyl ethers.
44. 1910 Cook, *THIS JOURNAL*, **32**, 1285 (98, 1, 731).  
A study of the bromination of phenyl and tolyl ethers.
45. 1910 Sabatier and Mailhe, *Compt. rend.*, **151**, 492 (98, 1, 669).  
Manufactured phenyl ether and its homologs by the use of thorium oxide as a catalytic agent.
46. 1910 Bonneaud, *Bull. soc. chim.*, [IV] **7**, 776 (98, 1, 669).  
A study of the action of bromine in the presence of aluminum bromide, on the phenyl ethers and their homologs.
47. 1910 Farb. v. Friedr. Bayer & Co. (98, 1, 312, 373).  
A description of the preparation of dyes from some diazotized aromatic amino ethers.
48. 1911 Cook, *THIS JOURNAL*, **33**, 254.  
An addenda to No. (44) containing omitted material.
49. 1911 Borsche and Rautscheff, *Ann.*, **379**, 152 (100, 1, 329).  
A study of the reaction of chloronitro benzene in which they prepared 2:6-dinitrophenyl ether.
50. 1912 Mailhe and Murat, *Bull. soc. chim.*, **154**, 122-3 (1912, 1-183).  
Made a study of the decomposition of phenyl ether by hydrogen in the presence of heated nickel.
51. 1912 Mailhe and Murat, *Compt. rend.*, **154**, 601 and *Bull. soc. chim.*, [IV] **11**, 288 (102, 1, 254).  
A study of the halogen derivatives of phenyl and ditolyl ethers.
52. 1912 Mailhe and Murat, *Compt. rend.*, **154**, 715 (102, 1, 346).  
A study of the nitration of phenyl ether.
53. 1912 Mailhe, *Compt. rend.*, **154**, 1240 (102, 1, 548).  
A description of the dyes obtained by treating diazotized *p*-amino phenyl ether with various compounds.
54. 1912 Sabatier and Mailhe, *Compt. rend.*, **155**, 260 (102, 1, 767).  
An extension of previous studies, several new compounds being produced.
55. 1914 Nollau and Daniels, *THIS JOURNAL*, **36**, 1885 (106, 1, 1129).  
A study of the reaction of the alkaline salts of sulfonic acids with the alkaline phenolates resulting in the preparation of various aromatic ethers.
56. 1915 Cook and Sherwood, *THIS JOURNAL*, **37**, 1835 (108, 1, 877).  
Made a number of new derivatives of phenyl ether.

MITCHELL, S. DAKOTA.

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[CONTRIBUTIONS FROM THE SHEFFIELD CHEMICAL LABORATORY OF YALE UNIVERSITY.]  
**RESEARCHES ON THIOCYANATES AND ISOTHIOCYANATES.<sup>1</sup>**  
**IX. ETHYL ISOTHIOCYANACETATE.**

By TREAT B. JOHNSON AND E. HEATON HEMINGWAY.

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Organic combinations containing the primary halide grouping  $\text{ClCH}_2$ -

<sup>1</sup> *Am. Chem. J.*, **26**, 345 (1901); **28**, 121 (1902); **33**, 448 (1905); **38**, 456 (1907); **40**, 132 (1908); last paper, *Ibid.*, **41**, 337 (1909); *THIS JOURNAL*, **23**, 283 (1901); **24**, 439, 680, 743 (1902); **25**, 483 (1903); **28**, 1454 (1906).

CO— are characterized by their behavior towards potassium thiocyanate. They interact with this salt with formation of normal thiocyanates, and in no case, which has been carefully investigated, has it been demonstrated that mustard oils are products of the reaction. Furthermore, it has never been shown, so far as the writers are aware, that thiocyanates of the type  $\text{NCS.CH}_2\text{CO.R}$  can be rearranged by heat into the isomeric mustard oils  $\text{SCNCH}_2\text{CO.R}$ . Such transformations have been assumed to take place by different investigators and also the reverse change,  $\text{SCN.CH}_2\text{COR} \rightarrow \text{NCS.CH}_2\text{COR}$ , but a careful reëxamination of their work has been productive of evidence, in every case investigated, that such conclusions are incorrect. Changes of an entirely different nature have been observed to take place, and they do not involve a migration of the polyketide group  $\text{—CH}_2\text{CO.R}$  from sulfur to nitrogen of the SCN radical.<sup>1</sup>

Recent developments in this laboratory<sup>2</sup> have now directed our attention again to the chemistry of these polyketide mustard oils. In connection with our work on polypeptide-hydantoins we have foreseen the possibility of utilizing certain combinations of this type for coupling with  $\alpha$ -aminoacids and consequently it was necessary to have available a practical method whereby they can be obtained in quantity for synthetical purposes. Such a method of synthesis has now been developed and in this paper we shall give a description of its application for the preparation of ethyl isothiocyanacetate,  $\text{SCN.CH}_2\text{COOC}_2\text{H}_5$ . So far as we are aware, this is the first polyketide isothiocyanate (mustard oil) to be described in the literature whose constitution has been definitely established.

In 1890, P. Klason published an interesting paper entitled, "Ueber Senfölessigsäure und Thiohydantoin," in which he described the preparation of ethyl isothiocyanacetate. He states that it is formed by the action of thiophosgene or ethyl aminoacetate in ether solution and expressed the transformation by the following equation:



The reaction apparently was a smooth one and the ester was obtained in good yield, but from what we can learn from abstracts of his original publication nothing was done by him to establish its constitution. While the results of this work are recorded, to our knowledge, in three different journals,<sup>3</sup> the mustard oil is not listed in Richter's *Lexikon der Kohlenstoff Verbindungen* nor described in Beilstein's *Handbuch*. It was undoubtedly due to this omission that Wheeler, in 1901, was led to insert, in one

<sup>1</sup> See previous papers from this laboratory.

<sup>2</sup> Unpublished results.

<sup>3</sup> *Ofv. kongl. Vet.-a. .*, 87 (1890); *Chem. Ztg.*, 14, Rep. 200; *Chem. Zentr.*, 2, 344 (1890).

of his earlier papers on alkylthiocyanates,<sup>1</sup> the following statement: "The results, now at hand, show that neither isothiocyanacetic acid nor any of its derivatives have yet been prepared."

During this same year (1901), E. Fischer investigated the action of phosgene on ethyl aminoacetate and showed that they interact in toluene to form the urea (I).<sup>2</sup> Apparently he obtained no evidence of the formation of the isocyanate (II) corresponding to ethylisothiocyanacetate.



(I).



(II).

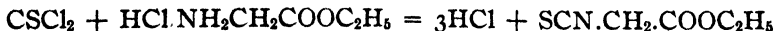
He did not take up the study of the action of thiophosgene on ethyl aminoacetate and furthermore makes no reference, in his paper, to the previous work of Klason. On the other hand, he attempted to convert the amino ester into ethyl isothiocyanacetate by combining it with carbon bisulfide and then breaking down the resulting dithiocarbamic acid salt (III) in the usual manner by digestion in aqueous solution with metallic salts. Fischer found that the salt (III) is formed smoothly, but the only evidence given in the paper indicating that an isothiocyanate was formed by its decomposition is the statement that the odor of mustard oil was apparent after digesting with mercury salts. Ethyl isothiocyanacetate was not isolated.



(III).

While ethyl aminoacetate interacts with phosgene to give the corresponding urea (I), the hydrochloride of this ester reacts with phosgene in an entirely different manner. Morel and Gautier<sup>3</sup> made the observation that they interact, when warmed in toluene, with evolution of hydrochloric acid and formation of the isocyanate (II). This reactive substance was obtained as an oil which could be distilled without decomposition, but was transformed by the action of water into the urea,  $\text{CO}(\text{NH}.\text{CH}_2\text{COOH})_2$ , originally obtained by Fischer.<sup>4</sup>

In the light of these developments it was of especial interest to investigate the behavior of thiophosgene towards the hydrochloride of ethyl aminoacetate. We now find that these substances interact at the temperature of boiling toluene giving Klason's ethyl isothiocyanacetate. In fact the yield is excellent and the ester can be synthesized in quantity without difficulty. We obtained no evidence of the formation of the thio-urea,  $\text{CS}(\text{NHCH}_2\text{COOC}_2\text{H}_5)_2$ . The reaction is expressed by the following equation:



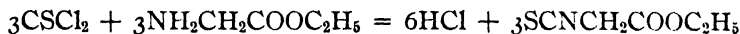
<sup>1</sup> Wheeler and Merriam, *THIS JOURNAL*, 23, 183 (1901).

<sup>2</sup> *Ber.*, 34, 440 (1901).

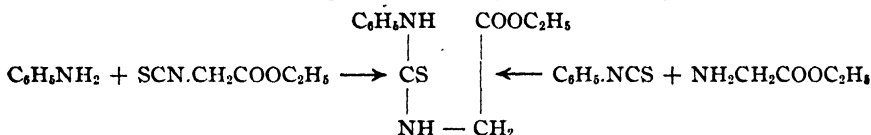
<sup>3</sup> *Compt. rend.*, 143, 119 (1906).

<sup>4</sup> *Loc. cit.*

From this result it is apparent that the equation formulated by Klason<sup>1</sup> to express the behavior of thiophosgene towards ethyl aminoacetate applies only when one molecular proportion of thiophosgene is used. The incorporation of an excess of thiophosgene would lead to a complete transformation of the aminoacetate into the corresponding isothiocyanate. Under these conditions the reaction would conform to the following expression:



Ethyl isothiocyanacetate boils at practically the same temperature as ethyl thiocyanacetate without undergoing a molecular rearrangement. It exhibits the properties of a true mustard oil and interacts with amines giving thiourea combinations or thiohydantoates. For example, it interacts with aniline giving the same thiohydantoate as was obtained by Fischer<sup>1</sup> by the action of phenylisothiocyanate on ethylaminoacetate.



Especially interesting was the behavior of this ester towards anhydrous ammonia. The isomeric ethyl rhodan acetate reacts with this reagent to form the corresponding amide<sup>2</sup>— $\text{NSC} \cdot \text{CH}_2\text{CO} \cdot \text{NH}_2$ . When a benzene solution of the ethyl isothiocyanacetate was saturated with ammonia gas at ordinary temperature the corresponding thiohydantoate (IV) was not formed as expected, but the mustard oil was converted practically quantitatively into 2-thiohydantoin (VI). This is a new method of entering the hydantoin series and the ease with which the hydantoin is formed at such a low temperature suggests that the thiohydantoate (IV) is not an intermediate product of the reaction. Harries and Weiss<sup>3</sup> were unable to convert this hydantoate into 2-thiohydantoin by hydrolysis. Klason<sup>1</sup> accomplished the transformation by heating the hydantoate at 140–150°. Johnson<sup>4</sup> recently confirmed this observation of Klason's but showed that the reaction is of no practical importance for the preparation of the thiohydantoin. It is not improbable that the ethyl isothiocyanacetate interacts with ammonia in a similar manner as its isomer (ethyl thiocyanacetate) with formation of the amide (V). If such a combination were formed it would be expected to undergo an inner condensation with formation of the 2-thiohydantoin (VI). A substituted acid amide (VII) on condensation would lead to the forma-

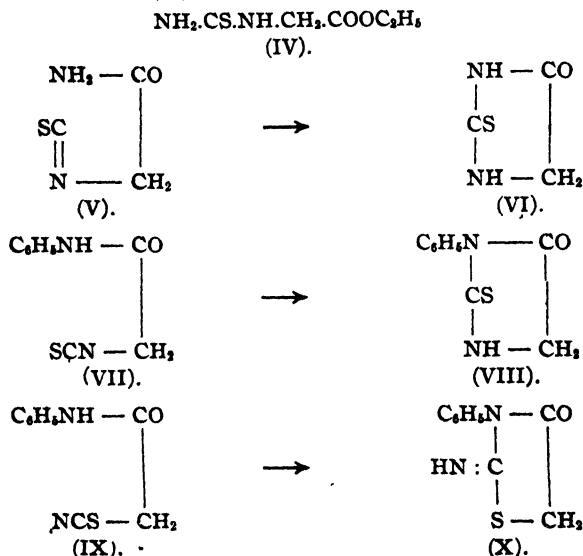
<sup>1</sup> *Loc. cit.*

<sup>2</sup> Claesson, *Ber.*, 10, 1346 (1877).

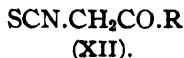
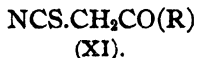
<sup>3</sup> *Ber.*, 33, 3418 (1900); *Ann.*, 327, 355.

<sup>4</sup> *THIS JOURNAL*, 35, 780 (1913).

tion 1-phenyl-2-thiohydantoin (VIII). It has been shown in a paper from this laboratory<sup>1</sup> that the corresponding anilides of rhodanacetic acid (IX) condense in an entirely different manner, giving pseudothiohydantoin combinations (X).



It is our intention to investigate the action of thiophosgene on other  $\alpha$ -aminoacids and to develop new reactions which will serve to distinguish polyketidethiocyanates (XI) from polyketideisothiocyanates (XII).



### Experimental Part.

**The Preparation of Thiophosgene,  $\text{CSCl}_2$ .**—All the thiophosgene used in our work was manufactured by reduction of tetrachloromethylmercaptan with stannous chloride according to the method of Kern and Sandoz.<sup>2</sup> The tetrachloromethylmercaptan was prepared by chlorination of carbon bisulfide.<sup>3</sup> We have prepared several thousand grams of this reagent this year, and have in progress several researches dealing with its application for synthetical purposes. The operation is carried on in the following manner: Five pounds of carbon bisulfide, to which is added about 5 g. of iodine as a catalyzer, are placed in a large bottle and cooled with ice-water. This bottle is connected with a condenser and the operation conducted in a hood. Chlorine gas from a bomb is then passed rapidly into the bisulfide until the increase in weight corresponds to 5 atomic

<sup>1</sup> Wheeler and Johnson, *Am. Chem. J.*, 28, 121 (1902).

<sup>2</sup> *Jahresbr.*, 1887, 2545; *Mo.ii. scientif.*, [4] 1, 1328.

<sup>3</sup> P. Klason, *Ber.*, 20, 2376 (1887).



proportions of the halogen. The crude reaction product is then washed by pouring into a tall, cylindrical glass retort and allowing water to circulate through the oil from the bottom. By running a constant stream of cold water beneath the oil and allowing to rise through it the sulfur halides are slowly decomposed and the soluble material gradually carried away. The tetrachloromethylmercaptan is thus obtained as a heavy oil and can be tapped off and distilled with steam to remove the last traces of sulfur halides. This last operation was applied twice and the mercaptan derivative then heated at  $142^{\circ}$  in an oil bath to remove carbon tetrachloride. This crude tetrachloromethylmercaptan was then used for the preparation of thiophosgene. From 5 pounds of carbon bisulfide we obtained 4.5 pounds of the tetrachloride. In order to prepare thiophosgene, 1.5 pounds of this tetrachloride were reduced at a time when we obtained from the 4.5 pounds of mercaptan 2.33 pounds of thiophosgene, corresponding to 84% of a theoretical yield. This was then bottled and used as needed in our research.

**Preparation of the Hydrochloride of Ethyl Aminoacetate,  $\text{HCl} \cdot \text{NH}_2\text{-CH}_2\text{COOC}_2\text{H}_5$ .**—All the ester used was prepared by esterification of methyleneaminoacetonitrile according to the directions of Klages.<sup>1</sup> Since potassium cyanide was not available we utilized commercial sodium cyanide for the manufacture of the nitrile. The modified procedure was not productive of as good yields as those obtained by Klages when potassium cyanide was used. The sodium cyanide seemed to favor the formation of the lower melting modification of methyleneaminoacetonitrile (m.  $86\text{--}87^{\circ}$ ). From 6000 g. of commercial 40% formaldehyde we obtained 853 g. of methyleneaminoacetonitrile melting at  $127\text{--}128^{\circ}$  and 328 g. of the lower melting modification. By hydrolysis of the 853 g. of methyleneaminoacetonitrile with alcohol and hydrochloric acid we obtained 1004 g. of the hydrochloride of ethyl aminoacetate.

**The Action of Thiophosgene on the Hydrochloride of Ethyl Aminoacetate. The Formation of Ethyl Isothiocyanacetate,  $\text{SCN} \cdot \text{CH}_2\text{COOC}_2\text{H}_5$ .**—This mustard oil is formed by the action of thiophosgene on the hydrochloride in either benzene or toluene solution. The yield is about 20 per cent. of theory when benzene is used and 50–60% when toluene is employed. Four hundred and twenty-five grams of the hydrochloride of ethylaminoacetate suspended in 600 cc. of toluene were heated in an oil bath at  $110\text{--}115^{\circ}$ , and 405 g. of thiophosgene (slightly more than one molecular proportion) added in small quantities during the course of eight hours. This mixture was then boiled gently for about one day in order to complete the reaction. There was still unaltered hydrochloride present after this treatment. This was separated by filtration and dried in the

<sup>1</sup> *Ber.*, 36, 1507 (1903).

air. It weighed 68 g. This was suspended again in fresh toluene and heated with an excess of thiophosgene in order to convert it completely into the mustard oil. After the reaction was complete the toluene was removed by heating at  $100^{\circ}$  under diminished pressure, when the isothiocyanate was obtained as a dark-colored oil. This new mustard oil was purified by distillation under diminished pressure. It boiled at  $112-113^{\circ}$  at 12 mm. and the yield corresponded to 60% of theory. In two other experiments our product boiled at  $110^{\circ}$  at 10 mm. and  $113^{\circ}$  at 15 mm. From 874 g. of the hydrochloride and 2.3 pounds of thiophosgene we obtained in all 642 g. of pure distilled isothiocyanate. This is a yield of 70% of the theoretical calculating from the weight of the hydrochloride used. In other words, from 5 pounds of carbon bisulfide, 11.6 pounds of chlorine and 6000 g. of 40% formaldehyde were produced 642 g. of mustard oil. This oil is colorless when first distilled, but turns red on standing. Under atmospheric pressure it boils at  $215^{\circ}$  with partial decomposition. Its density is 1.1710 at  $20^{\circ}$  (Westphal) and its refractive index is  $n_D^{20} = 1.5038$  (Abbe) and 1.5028 (Pulfrich).

Calc. for  $C_6H_7O_2NS$ : N, 9.67%. Found: N, 9.73, 9.41.

**The Action of Ammonia on Ethyl Isothiocyanacetate. The Formation of 2-Thiohydantoin.**—Five grams of ethyl isothiocyanacetate were dissolved in 50 cc. of benzene and dry ammonia gas passed through the solution for one hour. There was an immediate reaction and during the operation a crystalline product separated from the benzene. This was identified as 2-thiohydantoin. It was purified by crystallization from alcohol and melted at  $227^{\circ}$  with decomposition. To further establish its identity it was mixed with 2-thiohydantoin prepared according to the method described by Johnson and Nicolet<sup>1</sup> and a melting point taken. The mixture and the pure hydantoin melted at exactly the same temperature.

#### Behavior of Ethyl Isothiocyanacetate towards Aromatic Amides.

**Action of Aniline: Ethyl 1-Phenylthiohydantoate,  $C_6H_5.NH.CS.NH.CH_2COOC_2H_5$ .**—Two and two-tenths grams of ethyl isothiocyanacetate and 1.4 grams of aniline were dissolved in 60 cc. of ether and the mixture digested on the water bath for several hours. On allowing the ether to evaporate spontaneously the above hydantoate was obtained in a crystalline condition. It crystallized from ether in the form of plates and melted at  $89^{\circ}$  to an oil. Fischer<sup>2</sup> prepared this same compound by the action of phenylisothiocyanate on ethyl aminoacetate and assigned to it a melting point of  $85^{\circ}$ .

Calc. for  $C_{11}H_{14}O_2N_2S$ : N, 11.74%. Found: N, 11.58, 11.51.

**Ethyl *p*-Tolylthiohydantoate,  $CH_3C_6H_4NHCSNHCH_2COOC_2H_5$ .**—This

<sup>1</sup> THIS JOURNAL, 33, 1974 (1911).

<sup>2</sup> *Loc. cit.*

was easily obtained by action of *p*-toluidine on ethyl isothiocyanacetate. It was purified by crystallization from ether and alcohol and separated in long needles which melted at 96°. The hydantoate is soluble in benzene, ether and alcohol and insoluble in water.

Calc. for  $C_{12}H_{16}O_2N_2S$ : N, 11.13%. Found: N, 11.01, 10.96.

**Ethyl *o*-Tolylthiohydantoate**,  $CH_3C_6H_4NHCSNHCH_2COOC_2H_5$ .—From *o*-toluidine and ethyl isothiocyanacetate. The compound is soluble in alcohol and ether and insoluble in water. It melts at 90°.

Calc. for  $C_{12}H_{16}O_2N_2S$ : N, 11.13%. Found: N, 11.00, 10.97.

**Ethyl *m*-Tolylthiohydantoate**,  $CH_3C_6H_4NHCSNHCH_2COOC_2H_5$ .—From *m*-toluidine and ethyl isothiocyanacetate. It crystallizes from alcohol or ether in the form of prismatic needles and melts at 97°.

Calc. for  $C_{12}H_{16}O_2N_2S$ : N, 11.13%. Found: N, 11.25, 11.21.

**Ethyl *p*-Nitrophenylthiohydantoate**,  $NO_2.C_6H_4NHCSNHCH_2COOC_2H_5$ .—This ester crystallizes from alcohol in the form of light yellow needles arranged in rosetts. It melts at 191.5°.

Calc. for  $C_{11}H_{13}O_4N_3S$ : N, 14.87%. Found: N, 14.82, 15.00.

**The Action of Thiophosgene on the Hydrochloride of Glycocoll**.—Twenty grams of the hydrochloride of glycocoll were suspended in 60 cc. of toluene and 22 g. of thiophosgene added to the toluene. The mixture was then digested for two days at 110–115°. The unaltered hydrochloride was then separated by filtration and dried. Practically the whole amount taken was recovered unaltered.

NEW HAVEN, CONN.

[CONTRIBUTIONS FROM THE SHEFFIELD CHEMICAL LABORATORY OF YALE UNIVERSITY.]

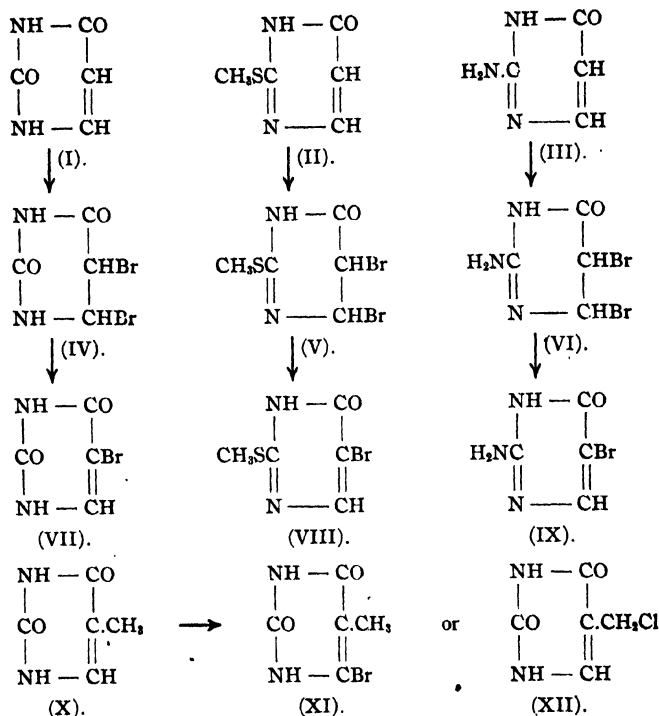
## RESEARCHES ON PYRIMIDINES. LXXX. THE MECHANISM OF THE ACTION OF BROMINE ON 2-MERCAPTOPYRIMIDINES.

By TREAT B. JOHNSON AND A. WILLARD JOYCE.

Received June 17, 1916.

It is known that 6-oxypyrimidines of the three types represented by uracil (I), 2-methylmercapto-6-oxypyrimidine (II), and isocytosine or 2-amino-6-oxypyrimidine (III), interact, respectively, with chlorine, bromine and iodine with substitution of one hydrogen atom of the pyrimidine ring by halogen. Wheeler and Bristol<sup>1</sup> showed that the 5-position of the pyrimidine ring is the point of attack in such reactions leading to the formation of the corresponding 5-halogenated pyrimidines (VII, VIII and IX). These transformations, when bromine is used, are represented by the following formulas:

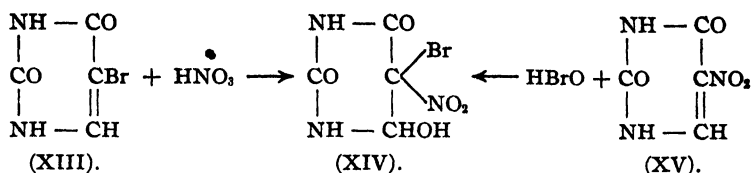
<sup>1</sup> *Am. Chem. J.*, **33**, 437 (1905); Johnson and Johns, *Ibid.*, **34**, 175 (1905); *J. Biol. Chem.*, **1**, 305 (1905).



When the 5-position of the ring in these series is occupied by an alkyl group ( $\text{CH}_3^-$ ,  $\text{C}_2\text{H}_5^-$ , etc.) and the 4-position is unsubstituted as, for example, in the case of thymine (X), the pyrimidine shows no tendency to interact with halogens, under normal conditions, with formation of halogen derivatives substituted in the 4-position (XI), or even in the side chain (XII), as is observed to take place with the higher homologs of benzene. The behavior of thymine towards halogens at high temperatures has not been investigated.

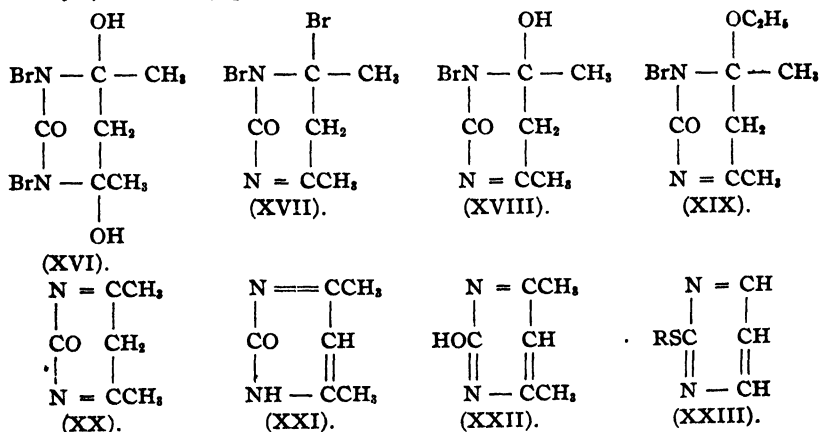
All these transformations very probably involve primarily an addition of bromine to the double bond of the pyrimidine ring giving unstable combinations (IV, V and VI), which then break down with formation of hydrobromic acid and 5-bromopyrimidines. In no case, however, has a halogen addition product of this type been isolated in these series. On the other hand, it has been shown that 2,6-dioxypyrimidines (thymine) readily combine with hypochlorous, hypobromous and even nitric acid giving stable addition products. For example, 5-bromouracil (XIII) and 5-nitouracil (XV) interact with concentrated nitric acid and hypobromous acid, respectively, giving the same hexahydropyrimidine (XIV).<sup>1</sup>

<sup>1</sup> Johnson, *Am. Chem. J.*, 40, 19, (1908).



Our knowledge of the action of halogens on 2-oxypyrimidines (XX), is very limited while the behavior of these elements towards the corresponding 2-mercaptopyrimidines (XXIII) has never been investigated. Evans<sup>1</sup> was the first to investigate the action of halogens on 2-oxypyrimidines and showed that 2-oxy-4,6-dimethylpyrimidine (XX) interacts with bromine water, giving a hexahydropyrimidine to which he assigned the constitution (XVI). This reaction was later reinvestigated by Stark<sup>2</sup> who made the interesting observation that this ketopyrimidine (XX) readily adds bromine in chloroform, forming an addition product which is unstable in the presence of water and alcohol. He assigned to this addition product the constitution XVII, and represented the products formed by treatment with water and alcohol according to Formulas XVIII and XIX. In other words, this pyrimidine, which is both acidic and basic in character and consequently can react in a tautomeric manner, adds bromine to the unsaturated group  $-\text{N} = \text{C}.\text{CH}_3$  instead of the ethylene group-

ing in positions 4 and 5 of the ring, as represented in the two tautomers of 2-oxy-4,6-dimethylpyrimidine (XXI) and (XXII).



In the light of these results it was of great interest to investigate the action of bromine towards 2-mercaptopyrimidines as represented by the general Formula XXIII. Compounds of this type are basic in character and cannot react in a tautomeric manner. In other words, they

<sup>1</sup> *J. prakt. Chem.*, 48, 489 (1893).

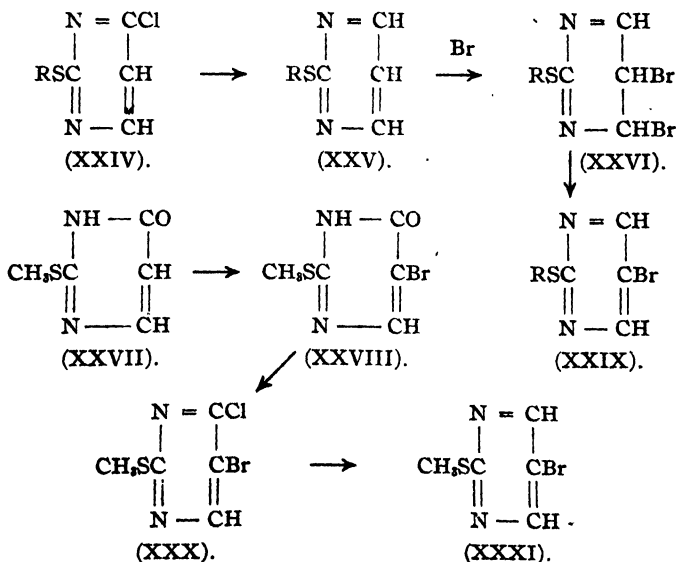
<sup>2</sup> *Ber.*, 42, 708 (1909).

do not contain a mobile hydrogen atom and consequently can be assigned only one constitution. This corresponds with that represented by the tautomeric formula of 2-oxy-4,6-dimethylpyrimidine (XXII).

We have now investigated the action of bromine on 2-methylmercaptopyrimidine and 2-ethylmercaptopyrimidine<sup>1</sup> (XXV). These two mercapto bases were prepared by reduction of their corresponding 2-mercapto-6-chloropyrimidines (XXIV). We find that both these pyrimidines add bromine quantitatively in carbon tetrachloride solution, forming addition products (XXVI) insoluble in this solvent. The 2-methylmercapto compound is a solid while its higher homolog was always obtained as a dark colored oil. In other words, the transformation of 2-mercapto-6-oxyprymidines into 2-mercaptopyrimidines is productive of greater unsaturation within the molecule, and the valency-force of the unsaturated ethylene grouping between positions 4 and 5 is greatly increased.

These addition products are the first representatives of a new class of dihydropyrimidines and are characterized by very unique properties. They easily undergo dissociation when warmed with water or dilute alkali, with regeneration of the original mercaptopyrimidines. This same change is also brought about quantitatively by the action of acetone. Both of the dihydropyrimidines (XXVI) interacted with this ketone at ordinary temperature with formation of bromoacetone and the hydrobromic acid salt of the original mercaptopyrimidines.

(R = CH<sub>3</sub> — and C<sub>2</sub>H<sub>5</sub> —.)



<sup>1</sup> Johnson and Joyce, *THIS JOURNAL*, 37, 2151 (1915).

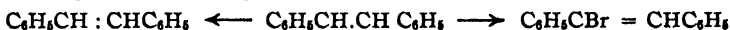
These changes are perfectly analogous to those which have been observed to take place with similar combinations in the acyclic series. For example, Erlenmeyer and Muller<sup>1</sup> observed that  $\alpha,\beta$ -dibromobutyric acid (XXXII) easily loses bromine when warmed in aqueous solution with potassium iodide with formation of crotonic acid (XXXIII) and iodine.



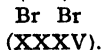
(XXXII).

(XXXIII).

Especially interesting in this connection are observations of Pfeiffer<sup>2</sup> on the behavior of the asymmetric isomers or dibromostilbene and related compounds towards pyridine. While the  $\beta$ -modifications of dibromostilbene, (XXXV) and  $\beta$ -dinitrodibromostilbene (XXXVIII) interact with this reagent, on warming, to give the corresponding unsaturated monohalides represented by Formulas XXXVI and XXXIX, the  $\alpha$ -modifications, on the other hand, behave in an entirely different manner. They undergo dissociation in presence of the same reagent with formation of stilbene (XXXIV) and dinitrostilbene (XXXVII), respectively. These changes may be represented as follows:



(XXXIV).

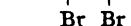


(XXXV).

(XXXVI).



(XXXVII).



(XXXVIII).

(XXXIX).

So far as the writers are aware the behavior of such combinations towards acetone has never been investigated.

When the addition products (XXVI) are heated under pressure, hydrobromic acid is evolved and halogenated mercaptopyrimidine (XXIX) is obtained containing bromine in position 5 of the pyrimidine ring. The structure of the bromine derivative (XXXI), which was obtained by heating its corresponding methylmercapto addition product (XXVI), was established as follows: 2-methylmercapto-6-oxypyrimidine<sup>3</sup> (XXVII) was prepared and combined with bromine, when the bromopyrimidine (XXVIII) was easily formed. This was then converted into the pyrimidine (XXX) by interaction with phosphorus oxychloride. When this bromochloropyrimidine was reduced with zinc dust, the chlorine atom only was replaced by hydrogen and 2-methylmercapto-5-bromopyrimidine (XXXI) was obtained. This was identical with the bromopyrimidine

<sup>1</sup> *Ber.*, **15**, 49 (1882).

<sup>2</sup> *Ibid.*, **45**, 1810 (1912); **48**, 1048 (1915).

<sup>3</sup> Wheeler and Merriam, *Am. Chem. J.*, **29**, 478 (1903).

formed by heating the methylmercapto addition product (XXVI). Therefore *when 2-mercaptopyrimidines interact with bromine they form addition products, which break down on heating with substitution of the halogen in the 5-position of the pyrimidine ring.*

### Experimental Part.

**The Behavior of Bromine towards 2-Methylmercaptopyrimidine in Carbon Tetrachloride Solution: 2-Methylmercapto-4,5-dibromodihydropyrimidine (XXVI).**—The 2-methylmercaptopyrimidine used in this preparation was obtained by the reduction of 2-methylmercapto-6-chloropyrimidine.<sup>1</sup> Two grams of the 2-mercaptopyrimidine were dissolved in 20 cc. of carbon tetrachloride and the solution cooled with ice-water. To this were then added 3.5 grams of bromine dissolved in 20 cc. of cold carbon tetrachloride. The bromine which was used here was previously dried by washing with concentrated sulfuric acid. On mixing the above reagents a turbidity was produced and after standing a short time clusters of red needles deposited on the sides of the flask. After standing about 15 minutes, when the reaction was apparently complete, these crystals of the addition product were filtered off quickly by suction, washed with carbon tetrachloride and finally dried over concentrated sulfuric acid in a vacuum desiccator. The crystals could not be exposed to the air for any prolonged time, the substance being decomposed by moisture. We obtained 3.75 g. of the addition product while a theoretical yield would be 4.15 g.

This pyrimidine is very unstable in the presence of moisture and even on warming in anhydrous solvents, so that we were not able to purify it by crystallization. It is insoluble in carbon tetrachloride, benzene and ether. It is decomposed by water, alkalis and acids, with formation of the original 2-mercaptopyrimidine. We were not able to assign a sharp melting point to the compound. It began to melt, when heated in a capillary tube, at 65°, giving finally a clear oil at 75°.

Calc. for  $C_5H_6N_2SBr_2$ : N, 9.79%. Found: N, 9.53, 9.58.

**The Action of Acetone on the Addition Product.**—The dihydropyrimidine interacts with acetone at ordinary temperature. When treated with this reagent the addition compound dissolves, giving a yellow solution which becomes colorless on stirring and finally deposits the original 2-methylmercaptopyrimidine in the form of its hydrobromic acid salt. At the same time bromoacetone is formed which is easily recognized by its odor and irritating action on the eyes. The hydrobromide of the pyrimidine base was purified by crystallization from absolute alcohol and melted at 188° with decomposition.

Calc. for  $C_5H_6N_2S \cdot HBr$ : N, 13.52%. Found: N, 13.7.

<sup>1</sup> Johnson and Joyce, *THIS JOURNAL*, 38, 1385 (1916).



This salt was decomposed by treatment with an aqueous solution of alkali and the free pyrimidine extracted with ether. After removal of the ether the pyrimidine was converted into a double platinum chloride salt, which proved to be identical with the platinum salt of the base described in our previous paper.<sup>1</sup> It melted at 207–208° with decomposition.

**Behavior of 2-Methylmercapto-4,5-dibromodihydropyrimidine on Heating: The Formation of 2-Methylmercapto-5-bromopyrimidine (XXXI).**—Four grams of the 2-methylmercaptopyrimidine were dissolved in 20 cc. of carbon tetrachloride and the solution transferred to a pressure tube. Five grams of bromine, dissolved in 20 cc. of carbon tetrachloride, were then added and the tube sealed. The addition product separated almost at once in a crystalline condition. The tube was then heated at 100° for 10 hours. There was no pressure when it was opened, and underneath the colorless tetrachloride was a layer of a dark colored oil. The carbon tetrachloride was poured off and the solvent evaporated under diminished pressure, when we obtained a yellow liquid which solidified on cooling. This material weighed 1 g. This was triturated with ether, in which most of it dissolved, but leaving a small amount of solid material which was very soluble in water. The latter product was identified as the hydrobromic acid salt of 2-methylmercapto-5-bromopyrimidine. On evaporating the ether solution a crystalline substance was obtained which was easily purified by crystallization from dilute alcohol or a mixture of acetone and water and deposited in the form of transparent plates melting at 64–65°. It was identified as 2-methylmercapto-5-bromopyrimidine. This pyrimidine is insoluble in water, dilute alkali and dilute acids, but soluble in alcohol, ether and acetone.

Calc. for  $C_5H_5N_2SBr$ : N, 13.65%. Found: N, 13.49.

In another experiment the dibromo addition product was heated in a pressure tube at 125–135° for 4 hours. Under these conditions there was much more decomposition and a larger proportion of the hydrobromic acid salt of the bromopyrimidine was formed. In place of the dark-colored oil obtained in the previous case there was formed a black decomposition product which was not examined further. When the tube was opened there was some pressure due to the presence of hydrobromic acid and a crystalline substance was suspended in the carbon tetrachloride. This material was identified as the hydrobromide of 2-methylmercapto-5-bromopyrimidine and melted at 205–206°. It dissolved in water with dissociation into hydrobromic acid and the free 2-methylmercaptobromopyrimidine. The latter crystallized from dilute alcohol in the form of plates and melted at 65–6°.

<sup>1</sup> Johnson and Joyce, *Loc. cit.*

**Experimental Proof of the Structure of the Mercaptobromopyrimidine: 2-Methylmercapto-5-bromo-6-oxypyrimidine (XXVIII).**—This new pyrimidine was prepared in a similar manner as that employed by Wheeler and Johnson<sup>1</sup> for the preparation of the corresponding 2-ethylmercaptopyrimidine. Our procedure was as follows: Ten grams of 2-methylmercapto-6-oxypyrimidine were dissolved in 60 cc. of glacial acetic acid and 11.2 g. of bromine (in 20 cc. of glacial acetic acid) added slowly through a dropping funnel. The bromopyrimidine began to separate very quickly. After final addition of the bromine the mixture was allowed to stand for 2 hours and the bromopyrimidine then separated by filtration. It was purified by crystallization from alcohol and separated, on cooling, in the form of needles which melted at 239° with decomposition. The yield of purified pyrimidine was 10.6 g. or 70% of the theoretical.

Calc. for  $C_6H_5ON_2SBr$ : N, 12.67%. Found: N, 13.00.

**2-Methylmercapto-5-bromo-6-chloropyrimidine (XXX).**—This chloropyrimidine was obtained by the action of phosphorus oxychloride on the above mercaptopyrimidine. Nine grams of the mercaptopyrimidine were suspended in 25 cc. of the phosphorus halide and the mixture heated in an oil bath at 125° for 2 hours. Hydrochloric acid was evolved and the pyrimidine dissolved completely. The excess of phosphorus oxychloride was then removed by heating at 100° under diminished pressure, when we obtained the pyrimidine in the form of a thick oil. This was triturated with cold water to destroy any phosphorus halide present and the pyrimidine then extracted with ether and dried over anhydrous calcium chloride. After removing the ether, the bromochloropyrimidine was obtained as an oil which solidified on cooling. It crystallized from ether in the form of needles and melted at 44° to an oil.

Calc. for  $C_6H_4N_2SClBr$ : N, 11.69%. Found: N, 11.72.

**Reduction of 2-Methylmercapto-5-bromo-6-chloropyrimidine with Zinc Dust. The Formation of 2-Methylmercapto-5-bromopyrimidine.**—Three grams of the mercaptopyrimidine were dissolved in 25 cc. of alcohol (95 per cent.) and the solution diluted with 25 cc. of water. To the slightly turbid solution 5 g. of zinc dust were added. There was an indication immediately that there was partial reduction, because the zinc dust assumed a granular or flaky condition. The mixture was digested under reflux condenser for 15 minutes, cooled and finally filtered to remove the excess of zinc. The alcohol and water were then removed by evaporation under diminished pressure, when we obtained an oil which was insoluble in water. This was dissolved in ether and dried over anhydrous calcium chloride. When the ether was evaporated an oil was obtained which did not solidify after standing for several days in a vacuum over sulfuric

<sup>1</sup> *Am. Chem. J.*, 31, 603 (1904).

acid. In order to isolate the 5-bromopyrimidine this oil was treated with concentrated hydrobromic acid, when the hydrobromide of the pyrimidine separated at once in a crystalline condition. On dissolving this in alcohol it underwent dissociation, and after cooling the solution the 2-methylmercapto-5-bromopyrimidine separated in the form of needles. They melted at  $65^{\circ}$  to an oil. The yield of this pyrimidine was 1 g.

Calc. for  $C_6H_6N_2SBr$ : N, 13.65%. Found: N, 13.60.

**The Addition of Bromine to 2-Ethylmercaptopyrimidine.**—Bromine combines with this pyrimidine in carbon tetrachloride solution at ordinary temperature. Two and three-tenths grams of bromine dissolved in 20 cc. of the tetrachloride were added to a cold solution of 2 g. of the pyrimidine in 20 cc. of carbon tetrachloride. The resulting mixture was then cooled to  $0^{\circ}$  with ice-water and allowed to stand for several hours at this temperature. The addition product did not separate in a crystalline condition as in the case of the 2-methylmercaptopyrimidine but deposited as a dark colored oil which showed no sign of crystallizing on standing. The carbon tetrachloride was removed by evaporation under diminished pressure and the oil again allowed to stand for several days in a desiccator, but it still showed no evidence of solidifying and was used for the following experiments:

**Action of Acetone and the Crude Addition Product. The Formation of 2-Ethylmercaptopyrimidine (XXV).**—This addition product interacts immediately with acetone at ordinary temperature, giving monobromoacetone and the hydrobromic acid salt of this pyrimidine. On mixing the two reagents and allowing to stand this hydrobromide deposits in the form of prisms. It was purified by crystallization from alcohol and melted at  $140-141^{\circ}$ . A mixture of this salt with that originally prepared by Johnson and Joyce<sup>1</sup> melted at the same temperature.

Calc. for  $C_6H_6N_2S.HBr$ : N, 12.67. Found: N, 12.35, 12.40.

**Conversion of the Addition Product into 2-Ethylmercapto-5-bromopyrimidine (XXIX).**—This new pyrimidine is formed by heating 2-ethylmercaptopyrimidine (2 g.) with the required amount of bromine in carbon tetrachloride solution for 10 hours at  $125-130^{\circ}$ . When the bomb tube was opened there was pressure due to the presence of hydrobromic acid and a dark tarry product adhered to the sides of the tube. Suspended in the tetrachloride was a considerable amount of material crystallized in the form of needles, which melted at  $180^{\circ}$  with decomposition. This was the hydrobromic acid salt of 2-ethylmercapto-5-bromopyrimidine. It was very soluble in water and on warming the solution immediately underwent dissociation. When the salt was dissolved in hot, dilute alcohol and the solution cooled the free base separated in the form of

<sup>1</sup> *Loc. cit.*

needles melting at  $43-5^{\circ}$  to an oil. The substance contained sulfur and bromine and a nitrogen determination agreed with the calculated value for 2-ethylmercapto-5-bromopyrimidine.

Calc. for  $C_6H_7N_2SBr$ : N, 12.78. Found: N, 12.90.

When the carbon tetrachloride was evaporated more of this same base was obtained and melted at  $43-45^{\circ}$ .

NEW HAVEN, CONN.

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[CONTRIBUTION FROM THE CARBOHYDRATE LABORATORY, BUREAU OF CHEMISTRY,  
UNITED STATES DEPARTMENT OF AGRICULTURE.]

## SOME NUMERICAL RELATIONS AMONG THE ROTATORY POWERS OF THE COMPOUND SUGARS.

By C. S. HUDSON.

Received June 8, 1916.

The general group of polysaccharides includes many pure crystalline substances of definite chemical individuality, such as the di-, tri-, and tetrasaccharides, together with a series of amorphous products, such as starch, glycogen, inulin, cellulose, pentosans, mannans, galactans, etc. To distinguish the pure crystalline polysaccharides from their less definitely characterized relatives, it is suggested that they be classed under the group name of *compound sugars*, a designation which separates them very well also from the simple sugars, or monosaccharides, into which they may be decomposed by hydrolysis. In the present article, it is sought to extend to several of the compound sugars the numerical relationships that have been found to hold among the rotatory powers of the alpha and beta forms of the monosaccharides and their glucosidic derivatives.<sup>1</sup>

### Sugars of the Sucrose Group.

**Known Members of the Group.**—The trisaccharide raffinose may be split by complete hydrolysis into its three component simple sugars, galactose, glucose and fructose; by partial hydrolysis, best through the agency of enzyme action, it may be split either into fructose and melibiose (= galactose < glucose <<sup>2</sup>) by the use of invertase or weak acids, or into galactose and sucrose (= glucose < > fructose) by the aid of emulsin. Raffinose may accordingly be regarded as galactose < glucose < > fructose, a derivative of sucrose, a combination between that sugar and galactose. Other sugars which are now regarded as derivatives of sucrose are<sup>3</sup> gentianose (= glucose < glucose < > fructose) and stachyose (= galactose <

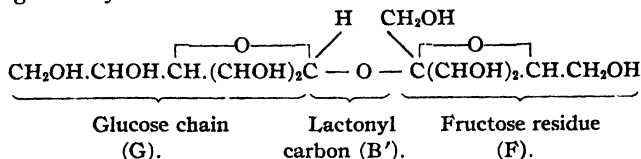
<sup>1</sup> THIS JOURNAL, 31, 66 (1909).

<sup>2</sup> The symbol < denotes the carbonyl or lactonyl group. See THIS JOURNAL, 31, 661 (1909). The term lactonyl, which has been suggested by S. F. Acree (*Science*, 42, 101 (1915)) to indicate an aldehyde or ketone group that has formed a lactone-like ring, as in the sugars, seems very appropriate.

<sup>3</sup> Bourquelot and Bridel, *Compt. rend.*, 152, 1060 (1911).

*galactose* < *glucose* > *fructose*). It will be convenient to designate sucrose and its three derived compound sugars as members of the sucrose group. The evidence that gentianose and stachyose belong in the group is not direct and conclusive as in the case of raffinose, though it appears convincing, as will be seen. The action of invertase upon either sucrose or raffinose causes specific hydrolysis of the union between glucose and fructose, which may be designated the *sucrose union*. Invertase may be regarded therefore, as a specific hydrolyst of the "sucrose union," and the action of this enzyme upon a compound sugar may be taken as evidence that the sugar contains the "sucrose union" and is a derivative of sucrose. Bourquelot and Hérissé<sup>1</sup> have shown that invertase splits gentianose into fructose and gentiobiose (= *glucose* < *glucose* <) and C. Tanret<sup>2</sup> has shown that it splits stachyose into fructose and manninotriose (= *galactose* < *galactose* < *glucose* <), hence these sugars are considered to be derivatives of sucrose. Recently Bourquelot and Bridel<sup>3</sup> have isolated a new crystalline compound sugar, verbascose, which is hydrolyzed by invertase to fructose and another sugar, not yet isolated; probably verbascose belongs in the sucrose group.

**Rotatory Relationships in the Sucrose Group.**—The fact that sucrose is not a reducing sugar indicates that the lactonyl hydroxyl groups of its two constituents are bound in glucosidic union, and the further fact that only one molecule of water per molecule of sucrose becomes combined during hydrolysis shows that the groups in question are joined with each other, because if the union were otherwise, two molecules of water per molecule of sugar would be used up. The same conclusion may be drawn from the fact that sucrose yields an octacetate and contains, therefore, eight hydroxyl groups per molecule. The structure of sucrose is accordingly generally considered to be



In this formula it is assumed that the lactonyl ring is upon the gamma carbon in both hexoses, which appears likely, but the following argument would not be affected if these rings should prove to be in other positions:<sup>4</sup> Let G represent the rotation due to the glucose chain, not including,

<sup>1</sup> *J. pharm. chim.*, [6] 13, 305 (1901).

<sup>2</sup> *Bull. soc. chim.*, 27, 955 (1902). See also Vintilesco, *J. pharm. chim.*, 30, 167 (1909).

<sup>3</sup> *Compt. rend.*, 151, 760 (1910).

<sup>4</sup> What really is assumed, as will be understood from the continuation, is that the glucose lactonyl ring in sucrose is upon the same carbon atom as in the case of the alpha and beta forms of glucose.

however, the asymmetric lactonyl carbon of rotation  $B'$ , and let  $F$  be the rotation of the fructose residue. Summing these values the molecular rotation of sucrose may be written  $[M]_S = G + B' + F$ . According to this plan the molecular rotations of the members of the sucrose group may be formulated as follows, when (Mb), (Gb) and (Mn) indicate the rotations of the melibiose, gentiobiose and manninotriose chains, respectively:

Parent sugar.	Hydrolytic products with invertase.	Molecular rotation of the parent sugar.
Sucrose (M.W. 342)	Glucose (180) + Fructose (180)	$G + B' + F$ (1)
Raffinose (504)	Melibiose (342) + Fructose	$(Mb) + B' + F$ (2)
Gentianose (504)	Gentiobiose (342) + Fructose	$(Gb) + B' + F$ (3)
Stachyose (666)	Manninotriose (504) + Fructose	$(Mn) + B' + F$ (4)

Subtracting the molecular rotation of sucrose from that of raffinose,  $[M]_R$ , gives

$$[M]_R - [M]_S = (Mb) - G. \quad (5)$$

The specific rotation of sucrose is  $+66.5$ , and its molecular rotation  $(66.5)(342) = +22700 = [M]_S$ . In the article first cited it was shown that  $G$  may be obtained as half the *sum* of the molecular rotations of the alpha and beta forms of glucose, which gives the value  $+11900$  if the specific rotations of the two forms of glucose are taken as  $113^1$  and  $19.^2$  Introducing these values in Equation 5 and transposing gives

$$(Mb) = [M]_R - 10800. \quad (6)$$

To pass now from (Mb) to the rotation of either the alpha or beta form of melibiose it is necessary to add the rotation of the end asymmetric lactonyl carbon atom of melibiose. It has been shown in the former article that the rotation of this carbon is equal to half the *difference* of the molecular rotations of the alpha and beta forms of glucose, or  $8460$ , hence the molecular rotations of the forms of melibiose are written:

$$\text{Molecular rotation of } \alpha\text{-melibiose} = (Mb) + 8460 = [M]_R - 2340$$

$$\text{Molecular rotation of } \beta\text{-melibiose} = (Mb) - 8460 = [M]_R - 19300$$

Similar equations with the same numerical terms express the same relation between the molecular rotations of gentiobiose and gentianose, and of manninotriose and stachyose. *For the sugars of the sucrose group that are hydrolyzed by invertase to yield fructose and an aldose, the molecular rotation of the aldose is less than that of its parent sugar by 2340 for its alpha form and 19300 for its beta modification.* The rotatory powers of melibiose, gentiobiose, and manninotriose may be calculated by this relation.

**The Rotation of Melibiose.**—Since the specific rotation of raffinose is  $+123$ , its molecular rotation is  $+62000$ , and the molecular rotations of the alpha and beta forms of melibiose are calculated from the foregoing relation to have the values  $+59700$  and  $+42700$ , respectively, and from

<sup>1</sup> Hudson and Yanovsky, forthcoming publication.

<sup>2</sup> Hudson and Dale, forthcoming publication.

these the specific rotations are found to be  $+175^{\circ}$  and  $+125^{\circ}$ . The latter value agrees almost exactly with Loiseau's<sup>1</sup> measurement of the initial specific rotation of  $\beta$ -melibiose (124), and recently E. Yanovsky and the writer,<sup>2</sup> in repeating the measurement, have obtained the same value as Loiseau. The alpha form of melibiose has never been prepared in a pure state and the only experimental value known for its specific rotation is that which Yanovsky and the author have found indirectly through a measurement of the increase in solubility of  $\beta$ -melibiose during its mutarotation. Our value is  $+179^{\circ}$ .<sup>2</sup> The agreement is very good in view of the indirectness of the experimental measurement.

**The Rotation of Gentiobiose.**—The specific rotation of gentianose is  $+31$ ,<sup>3</sup> hence its molecular rotation is  $+15600$  and the specific rotations of the alpha and beta forms of gentiobiose may be calculated by the method which has just been followed to be  $+39$  and  $-11$ , respectively. Bourquelot and Hérissé<sup>4</sup> record  $+9.8$  as the final specific rotation of gentiobiose, a value which refers to the equilibrium in solution between the alpha and beta forms of the sugar. By crystallizing gentiobiose from methyl alcohol they obtained a crystalline derivative of it containing two molecules of methyl alcohol of crystallization. This substance had an initial specific rotation in water of about  $+18$ , decreasing to  $+9.8$  (both numbers are referred to the solvent-free sugar, m. w. 342) on standing. By crystallizing gentiobiose from ethyl alcohol solution they prepared the crystalline sugar itself, which had a specific rotation of  $-6$  six minutes after dissolving, changing likewise to  $+9.8$  on standing. If one extrapolates as well as possible the value  $-6$  back through the first six minutes according to the rate of mutarotation that Bourquelot and Hérissé observed a value near the calculated  $-11$  is obtained. It would seem that the alpha form of melibiose which they evidently had in hand in the form of a compound with methyl alcohol of crystallization contained some of the beta modification.

**The Rotation of Manninotriose.**—The specific rotation of stachyose being  $+148$ ,<sup>5</sup> its molecular rotation is  $+98600$ , and hence the specific rotations of the alpha and beta forms of manninotriose are calculated to be  $+191$ , and  $+157$ , respectively. These rotations do not appear to have ever been measured but C. Tanret<sup>6</sup> records  $+167$  as the final specific rotation of manninotriose. This value lies between the calculated numbers, as should be the case, and is also at approximately the same position between them as in the case of glucose, melibiose and gentiobiose. The

<sup>1</sup> *Z. Ver. Zuckerind.*, **52**, 1050-9 (1903).

<sup>2</sup> Forthcoming publication.

<sup>3</sup> Bourquelot and Nardin, *Compt. rend.*, **126**, 280 (1898).

<sup>4</sup> *J. pharm. chim.*, [6] **16**, 418 (1902).

<sup>5</sup> Schulze and Planta, *Ber.*, **24**, 2705 (1890).

<sup>6</sup> *Bull. soc. chim.*, [3] **29**, 891 (1903).

ratio of the concentrations of the beta and alpha forms which are present at equilibrium is for glucose  $(113 - 52^3)/(52 - 19) = 1.8$ , for melibiose  $(175 - 143^3)/(143 - 124) = 1.6$ , for gentiobiose  $(39 - 10^3)/(10 + 11) = 1.3$ , and for manninotriose  $(191 - 167^1)/(167 - 157) = 2.4$ . If the final rotation of manninotriose were 169 rather than 167 the ratio would be the same as for glucose, and if it were 172 the ratio would be the same as for gentiobiose.

**Other Possible Members of the Sucrose Group.**—Since lactose, cellose, and maltose have structures in which the free lactonyl hydroxyl is a part of the glucose group, it is conceivable that these disaccharides might be united with fructose through a sucrose union to yield derivatives of sucrose. The expected specific rotations of these compounds can be calculated according to the preceding considerations. For example, since the specific rotation of  $\beta$ -lactose (m. w. 342) is  $+35$ , its molecular rotation is  $+12000$ , and the specific rotation of the hypothetical  $\alpha$ -lactose  $< > \alpha$ -fructose (m. w. 504) is calculated to be  $(12000 + 19300)/504 = +62$ .

**The Acetylated Sugars of the Sucrose Group.**—Referring back to the structural formula for sucrose, consider the rotation of sucrose octacetate. Its molecular rotation is the sum of a new quantity  $G'$ , which is the rotation of an acetylated glucose chain, plus  $B''$ , which may possibly be different in value from  $B'$ , plus  $F'$ , the rotation of an acetylated fructose residue. In the same way that  $G$  was obtained from the specific rotations of the alpha and beta forms of glucose  $G'$  may be found from those of the corresponding glucose pentacetates (m. w. 390), which have the values  $+102$  and  $+4$ , respectively, in chloroform solution.<sup>3</sup> Half of the sum of their molecular rotations is  $+20700 = G'$ , and half the difference is  $+19100$ , the latter being the rotation of the end asymmetric carbon in glucose pentacetate. The specific rotation of sucrose octacetate (m. w. 678) in chloroform is  $+59.6$ ,<sup>3</sup> and hence its molecular rotation is  $+40400$ . The molecular rotation of the glucose pentacetate chain is therefore 19700 less than that of sucrose octacetate or the molecular rotation of  $\alpha$ -glucose pentacetate is  $(19700 - 19100) = 600$  less than that of sucrose octacetate, while that of the  $\beta$ -pentacetate is  $(19700 + 19100) = 38800$  less. These numerical differences apply also to the molecular rotations of the corresponding acetylated derivatives of the pairs raffinose and melibiose, gentianose and gentiobiose, stachyose and manninotriose. The beta octacetates (m. w. 678) of melibiose and gentiobiose have the specific rotations  $+102^4$  and  $-5$ ,<sup>5</sup> respectively, in chloroform solution. From

<sup>1</sup> Final specific rotations of the sugars.

<sup>2</sup> Hudson and Dale, *THIS JOURNAL*, **37**, 1265 (1915).

<sup>3</sup> Hudson and Johnson, *Ibid.*, **37**, 2753 (1915).

<sup>4</sup> Hudson and Johnson, *Ibid.*, **37**, 2752 (1915).

<sup>5</sup> Zemplen, *Z. physiol. Chem.*, **85**, 402 (1913).



these data the specific rotations of the hendecacetates (m. w. 966 and formula  $C_{28}H_{21}(C_2H_3O)_{11}O_{16}$ ) of raffinose and gentianose in chloroform are calculated to be +112 and +43, respectively. Scheibler and Mittelmeier<sup>1</sup> have found +92 for crystalline raffinose hendecacetate in alcohol, but the value in chloroform is not known. It is probably higher than +92, because the specific rotation of sucrose octacetate in chloroform is +60 (see preceding) and in alcohol, +38.<sup>2</sup> Gentianose hendecacetate does not appear to have ever been prepared.

### Sugars of the Trehalose Group.

**Trehalose and Isotrehalose.**—Since trehalose is not a reducing sugar, combines with only one molecule of water per molecule of sugar during hydrolysis, and also forms an octacetate, its structure may be considered to be *glucose* < > *glucose*, the lactonyl hydroxyls being united with the elimination of water. The three possible combinations which fit this structure, assuming gamma-lactonyl rings, are  $\alpha$ -*glucose* < >  $\alpha$ -*glucose*, the  $\alpha,\beta$  form, or the  $\beta,\beta$  form. If G represents the rotation of the glucose chain, as before, and A' that of the asymmetric lactonyl carbon (+A' for the  $\alpha$ -glucoside form and -A' for the  $\beta$ ) the molecular rotations of the three combinations may be formulated:

$$\alpha,\alpha\text{-Trehalose} \dots\dots\dots G + A' + A' + G = 2G + 2A'$$

$$\alpha,\beta\text{-Trehalose} \dots\dots\dots G + A' - A' + G = 2G$$

$$\beta,\beta\text{-Trehalose} \dots\dots\dots G - A' - A' + G = 2G - 2A'$$

The value of 2G has already been found from the sum of the molecular rotations of the alpha and beta forms of glucose to be +23800, and hence the specific rotation of  $\alpha,\beta$ -trehalose (m. w. 342) is calculated to be +70. This value is entirely different from the observed specific rotation of trehalose, +197, hence the natural sugar is not the  $\alpha,\beta$  combination. Neither can it be the  $\beta,\beta$  form because it should then be less dextrorotatory than +70 since the value of -A' for the known  $\beta$ -glucosides is a quantity of considerable magnitude. On the other hand, the high dextrorotation of trehalose agrees well with what would be expected for  $\alpha$ -*glucose* < >  $\alpha$ -*glucose*. Assuming this to be the structure of the natural sugar, its molecular rotation ( $197 \times 342 = +67400$ ) is  $2G + 2A'$ , and since 2G is +23800, 2A' is +43600, and the molecular rotation of  $\beta,\beta$ -trehalose ( $2G - 2A'$ ) may be calculated to be -19800, and the specific rotation -58. Under the name *isotrehalose*, Fischer and Delbrück<sup>3</sup> have recently described a sugar of the trehalose type which they prepared by the saponification of crystalline *isotrehalose octacetate*, a substance which in its turn was made by the condensation of bromo-acetyl glucose. Isotrehalose was not obtained in a crystalline state and the amorphous sub-

<sup>1</sup> Ber., 23, 1443 (1890).

<sup>2</sup> Herzfeld, *Ibid.*, 13, 267 (1880).

<sup>3</sup> Ber., 42, 2776 (1909).

stance was not free from ash. Under such conditions the specific rotation of the impure material can only be considered as an approximate value of the rotation of the pure sugar. Fischer and Delbrück found  $-39$ , a value which strongly suggests that isotrehalose is  $\beta,\beta$ -trehalose. This view is supported by the fact that all other derivatives that have been prepared from bromo-acetyl glucose belong to the  $\beta$  series. It is also supported by the result of the following considerations, which indicate that the parent substance, *isotrehalose octacetate*, is a  $\beta,\beta$  form.

**Octacetates of the Trehalose Sugars.**—The relations which have just been derived among the rotations of the three trehaloses and the alpha and beta forms of glucose apply likewise to the fully acetylated derivatives of these five substances. Thus the molecular rotation of  $\alpha,\beta$ -trehalose octacetate may be regarded equal to the sum of the molecular rotations of the alpha and beta glucose pentacetates, which is known to be  $+41400$ , and its specific rotation (m. w. 678) in chloroform is calculated to be  $+61$ . The observed specific rotation of pure trehalose octacetate in chloroform is  $+162$ ,<sup>1</sup> which indicates again that trehalose is the  $\alpha,\alpha$  form. The specific rotation of the  $\beta,\beta$  form, or isotrehalose octacetate, is calculated from these two rotations, by the same method that was used with the sugars, to be  $-40$  in chloroform. Fischer and Delbrück found  $-17$  in benzene, a difference which may be due to the change of solvent, because trehalose octacetate rotates  $-162$  in chloroform and  $+171$  in benzene.<sup>2</sup>

**Other Compound Sugars of the Trehalose Type.**—It may be useful to indicate that the rotation of nearly all the possible sugars of this type may be calculated from existing data. As an illustration consider the tetrasaccharide *lactose*  $\langle \rangle$  *lactose*, a combination which E. Fischer and H. Fischer<sup>3</sup> have sought to prepare through the condensation of bromo-acetyl lactose. Since the alpha and beta forms of lactose (m. w. 342) rotate  $+86$  and  $+35$ , respectively, twice the molecular rotation of the lactose chain is  $+41400$ . Since the molecular weight of the tetrasaccharide is 666, the specific rotation of its  $\alpha,\beta$  form is calculated to be  $41400/666 = +62$ . Assuming that the asymmetric lactonyl carbons uniting the glucose residues have the same rotations that were found for them in trehalose,  $2A' = +44000$ , and hence the specific rotation of the  $\alpha,\alpha$  form of the tetrasaccharide is calculated to be  $(41400 + 44000)/666 = +128$ , and that of the  $\beta,\beta$  form  $(41400 - 44000)/666 = -4$ .

From the specific rotations of the alpha and beta lactose octacetates (m. w. 678),  $+54$  and  $-4$  in chloroform,<sup>4</sup> and the value  $+68500$  for the

<sup>1</sup> Hudson and Johnson, *THIS JOURNAL*, 37, 2752 (1915).

<sup>2</sup> Measured recently in this laboratory by Dr. J. M. Johnson.

<sup>3</sup> *Ber.*, 43, 2532 (1910).

<sup>4</sup> Hudson and Johnson, *THIS JOURNAL*, 37, 1273 (1915).

two lactonyl carbons (calculated as in the case of the trehalose octacetates), the specific rotation of the fully acetylated derivatives (m. w. 1255) of *lactose* < *lactose* may be calculated to be, for the  $\alpha, \beta$  form  $+33900/1255 = +27$ , for the  $\alpha, \alpha$  form  $(33900 + 68500)/1255 = +82$ , for the  $\beta, \beta$  form  $-28$ . The similar derivatives of maltose and cellose can be treated in the same way. The calculations are here indicated because the work of E. Fischer with H. Fischer, and Zemplén<sup>2</sup> appear to open a way for synthesizing these compounds of lactose, maltose and cellose, respectively, when sufficient material is available.

Lastly, the expected specific rotation of  $\beta, l\text{-arabinose}$  <  $\beta, l\text{-arabinose}$  (m. w. 282) may be calculated from the specific rotations of the alpha and beta forms of the sugar,  $+76$  and  $+184$ , respectively, to be  $((76 + 184) 150 + 44000^3)/282 = +294^\circ$ . This rotation is of interest because it appears to be the largest specific rotation that can be expected among the sugars from present data.

### The Related Rotations of Lactose and Cellose.

There are three disaccharides which have the general structure *glucose* < *glucose* <, namely, maltose, cellose and gentiobiose, and two of the composition *galactose* < *glucose* <, namely, melibiose and lactose. In these structures the place of attachment of the left hand glucose or galactose molecule is evidently its lactonyl carbon, but several points of union for the right hand glucose molecule are possible. Without more knowledge of this point of attachment for each of the compound sugars, it does not seem possible in general to obtain relations among their rotatory powers. However, there is one special case which can be adequately treated at present and it leads to an interesting relation between the rotations of lactose and cellose. The structures shown above indicate that for each point of attachment in the right hand glucoside residue, there can be four related sugars according as the left hand member is  $\alpha$ - or  $\beta$ -glucose, or  $\alpha$ - or  $\beta$ -galactose. To formulate the rotations of these forms let  $G$  and  $G_a$ , respectively, be the rotations of the left hand glucose and galactose chains,  $L$  that of their bound lactonyl carbons, and  $R$  that of the common right hand glucose residue. Since the free lactonyl group of this residue permits  $\alpha$  and  $\beta$  forms, let  $R$  refer throughout to the same one of these. The molecular rotations of the four structures are thus:

$$\begin{array}{ll}
 \alpha\text{-galactose} < \text{glucose} < = G_a + L + R & \beta\text{-galactose} < \text{glucose} < = G_a - L + R \\
 \alpha\text{-glucose} < \text{glucose} < = G + L + R & \beta\text{-glucose} < \text{glucose} < = G - L + R
 \end{array}$$


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$$\begin{array}{ll}
 \text{Difference } G_a - G & G_a - G
 \end{array}$$

<sup>1</sup> *Loc. cit.*

<sup>2</sup> *Ber.*, 43, 2536 (1910).

<sup>3</sup> The assigning of a positive rather than negative sign to 44,000 (= 2A), although the compound is a  $\beta$ -derivative, is made because the arabinose is the *levo* form. See *THIS JOURNAL*, 31, 72 (1909).

The differences are equal to each other, and as will be seen readily are also equal to the difference of the molecular rotations of the corresponding  $\alpha$  and  $\beta$  forms of galactose and glucose, or of methyl galactoside and methyl glucoside. We reach the conclusion, therefore, that if either of the *galactose* < *glucose* < sugars (melibiose or lactose) has a structure in which the right hand glucose residue is identical with the similar component of one of the *glucose* < *glucose* < sugars (maltose, cellose or gentiobiose) the pair of sugars, in case both are  $\alpha$ -glucosidic compounds or both beta, should differ in molecular rotation by the difference between the molecular rotations of the galactose and glucose chains. The difference in specific rotation of  $\beta$ -methyl galactoside ( $0^\circ$ ) and  $\beta$ -methyl glucoside ( $-32^\circ$ ) (of m. w. 194) is  $+32^\circ$ , which amounts to  $(32)(194)/342 = +18^\circ$  in the specific rotation of the disaccharides (m. w. 342). If  $+18$  be added to the specific rotation of the beta forms of maltose ( $+118$ )<sup>1</sup> and of gentiobiose ( $-11$ ) the sums,  $+136$  and  $+7$  do not agree with the rotations of either  $\beta$ -melibiose ( $+124$ ) or  $\beta$ -lactose ( $+35$ ). On the other hand, the rotation of  $\beta$ -cellose ( $+16$ )<sup>1</sup> plus  $18$  is equal to that of  $\beta$ -lactose ( $35$ ) almost exactly.

**The Rotations of the Octacetates of These Sugars.**—It is highly desirable to test in independent ways this conclusion, that lactose and cellose have the same structure for their common glucose residue, and that the galactose residue of one belongs to the same series (probably the  $\beta$ , judging from the low rotation of lactose) as the glucosidic glucose residue of the other. If the similarity does exist, it would be expected to extend to many derivatives of these sugars, and it should be possible to decide from a comparison of the rotations of each pair of derivatives whether the agreement that has been found to hold for the parent sugars is a general one and really has for its basis the assigned reason, or is an accidental agreement in the one case tested. The rotations in chloroform solution of the pure octacetates of the disaccharides in question are known, and a comparison of them appears to be of special value because in them the rotations of the individual asymmetric carbon atoms in the glucose residue are doubtless quite different from the values for the sugars themselves. The difference between the specific rotations of tetra-acetyl  $\beta$ -methyl galactoside ( $-13$ )<sup>1</sup> of m. w. 362, and the corresponding acetylated  $\beta$ -methyl glucoside ( $-18$ )<sup>2</sup> is  $+5$ , which corresponds to  $(5)(362)/678 = 3^\circ$  for the disaccharide octacetates. The addition of this value to the specific rotation of  $\beta$ -maltose octacetate ( $+63$ ) gives a sum entirely different from the rotation of the  $\beta$ -octacetate of either melibiose ( $+102$ ) or lactose ( $-4$ ). On the other hand, the rotations of the  $\beta$ -octacetates of both cellose ( $-15$ ) and gentiobiose ( $-5$ ) yields sums ( $-12$  and  $-2$ ).

<sup>1</sup> Hudson and Yanovsky, forthcoming publication.

<sup>2</sup> Hudson and Dale, *THIS JOURNAL*, 37, 1265 (1915).

which are near the rotation of  $\beta$ -lactose octacetate ( $-4$ ). The combination of this result with that obtained from the rotations of the sugars themselves, in which gentiobiose was clearly ruled out, gives strong evidence that the common glucose residues of lactose and cellose have identical structure.

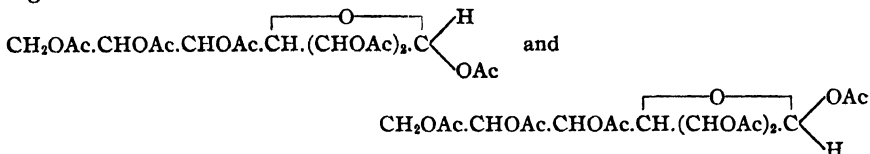
WASHINGTON, D. C.

## THE ISOMERIC ALPHA AND BETA HEXACETATES OF $\alpha$ -GLUCOHEPTOSE.

By C. S. HUDSON AND E. YANOVSKY.<sup>1</sup>

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E. Fischer<sup>2</sup> has shown that two isomeric fully acetylated derivatives of  $\alpha$ -glucoheptose could be prepared by the action of acetic anhydride on the sugar. When sodium acetate was used to catalyze the reaction, the crystalline product was a hexacetate which melted at  $132^\circ$ , but the use of zinc chloride gave an isomeric hexacetate of m. p.  $156^\circ$ . Fischer has mentioned that these isomeric hexacetates of  $\alpha$ -glucoheptose are produced by the same reactions which yield the alpha and beta pentacetates of glucose. Since the isomerism of the glucose pentacetates can be explained, according to Fischer,<sup>3</sup> as due to the existence of the structures that are now generally named the alpha and beta forms, it appears probable that the similarly produced hexacetates of  $\alpha$ -glucoheptose have the corresponding structures:



in which the asymmetry of the right-hand terminal carbon atom permits the two configurations. If this view is correct, the molecular rotatory power of the alpha form may be written  $+A + B'$ , and that of the beta form  $-A + B'$ , where  $A$  is the rotation of the terminal asymmetric carbon and  $B'$  is that due to the remainder of the structure.<sup>4</sup> It follows then that the difference of the molecular rotations of the two forms is  $2A$ , which is the same as the difference in the molecular rotations of the alpha and beta pentacetates of glucose, of rotations  $+A + B$  and  $-A + B$ , respectively. The rotations of the  $\alpha$ -glucoheptose hexacetates are not recorded in Fischer's article, and we have consequently prepared the sub-

<sup>1</sup> Contribution from the Carbohydrate Laboratory, Bureau of Chemistry, United States Department of Agriculture.

<sup>2</sup> *Ann.*, 270, 64 (1892); *Ber.*, 26, 2400 (1893).

<sup>3</sup> *Ber.*, loc. cit.

<sup>4</sup> Hudson, *THIS JOURNAL*, 31, 66 (1909).

stances in pure condition and have found the following rotatory powers in chloroform:<sup>1</sup>

$$\begin{array}{l} \alpha\text{-Hexacetyl } \alpha\text{-glucoheptose, } [\alpha]_D^{20} = +87.0, [M]_D^{20} = +40,200^2 = +A + B' \\ \beta\text{-Hexacetyl } \alpha\text{-glucoheptose, } [\alpha]_D^{20} = +4.8, [M]_D^{20} = +2,200 = -A + B' \end{array}$$

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$$\text{Difference} = 38,000 = 2A$$

The corresponding values for the glucose pentacetates in the same solvent have been found<sup>3</sup> to be

$$\begin{array}{l} \alpha\text{-Pentacetyl glucose, } [\alpha]_D^{20} = +101.6, [M]_D^{20} = +39,600^2 = +A + B \\ \beta\text{-Pentacetyl glucose, } [\alpha]_D^{20} = +3.8, [M]_D^{20} = +1,500 = -A + B \end{array}$$

$$\text{Difference} = 38,100 = 2A$$

The agreement of the values for 2A is a close one, the discrepancy of 100 amounting to only about 0.25° in specific rotation, which is well within the limits of experimental error. There is thus good evidence that the two hexacetates constitute an alpha and beta pair, and this is supported by the fact, which is described later on, that the lower rotating one may be readily transformed into the other by warming it in acetic anhydride solution with a little zinc chloride, a method which has been found in general to change beta acetates to the corresponding alpha isomers. Since  $\alpha$ -glucoheptose is a derivative of *d*-glucose, its more dextro-rotatory hexacetate ( $[\alpha]_D^{20} = +87^\circ$ ) is to be named<sup>4</sup> the alpha form, and the other ( $[\alpha]_D^{20} = +5$ ) the beta modification.

### Experimental.

**Preparation of the Beta Hexacetate of  $\alpha$ -Glucoheptose.**—A mixture of one part anhydrous sodium acetate, four parts  $\alpha$ -glucoheptose, and 16 parts acetic anhydride was heated until the sugar dissolved, and then poured into an excess of cold water. An insoluble sirup precipitated and soon crystallized, crystals also separating from the solution. On recrystallizing the product from hot water a yield equal to 75% of the weight of sugar taken was obtained. Recrystallization from 50% alcohol is a more effective way to obtain the beta hexacetate entirely free from the alpha isomer. After two recrystallizations from this solvent, the material showed the specific rotation of  $[\alpha]_D^{20} = +4.8$  in chloroform, a value which did not change with further recrystallization. The substance melted at 135°, uncorrected. Its elementary composition has been established by Fischer. For the acetyl determination, samples of 0.3092 and 0.2680 g. were boiled with 50 cc. 0.25 *N* H<sub>2</sub>SO<sub>4</sub> three hours in a quartz flask with

<sup>1</sup> *Chloroformum purificatum*, U. S. P., was used in all the measurements of the rotations.

<sup>2</sup> The molecular weight of the hexacetate is taken as 462, that of glucose pentacetate 390.

<sup>3</sup> Hudson and Dale, *THIS JOURNAL*, 37, 1264 (1915).

<sup>4</sup> See *THIS JOURNAL*, 31, 72 (1909).

a quartz reflux condenser, yielding 55.6 and 56.0% acetyl ( $\text{CH}_3\text{CO}$ ) in comparison with 55.8, the calculated value for a heptose hexacetate.

**Preparation of the Alpha Hexacetate of  $\alpha$ -Glucoheptose.**—Since it has already been shown by Fischer that this isomer is produced through the acetylation of the sugar with hot acetic anhydride and zinc chloride, we sought to obtain it by a method which has frequently been used in this laboratory to prepare alpha acetates, namely, by heating the acetic anhydride solution of the beta acetate with a little zinc chloride. Ten grams of the beta hexacetate were dissolved in 100 cc. acetic anhydride containing 2 g.  $\text{ZnCl}_2$ . The specific rotation of this solution was  $-10^\circ$  to begin with, but after heating it three hours on the steam bath its rotation became constant at  $+25$ , indicating that the equilibrium in this solvent between the alpha and beta forms of the hexacetate had been established. On pouring the mixture into cold water an insoluble sirup precipitated and soon crystallized. The aqueous solution was extracted with chloroform, the extract washed with sodium bicarbonate solution and with water, and the crystals which formed when the chloroform was evaporated were united with those from the insoluble mass. One recrystallization from hot water of this product yielded crystals which had a specific rotation of  $+32$ , but on recrystallizing then five times from ether, a constant specific dextrorotation of  $+87.0^\circ$  in chloroform was found. The pure substance melted at  $164^\circ$ , uncorrected, which is higher than the value found by Fischer,  $156^\circ$ , but our material was probably more nearly free from the beta isomer. Two acetyl estimations gave 55.6 and 55.5%  $\text{CH}_3\text{CO}$  in comparison with the calculated value 55.8.

WASHINGTON, D. C.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

## TRIPHENYLMETHYL. XXVI. TAUTOMERISM OF TRIARYL-CARBINOLS.

BY M. GOMBERG AND N. E. VAN STONE.

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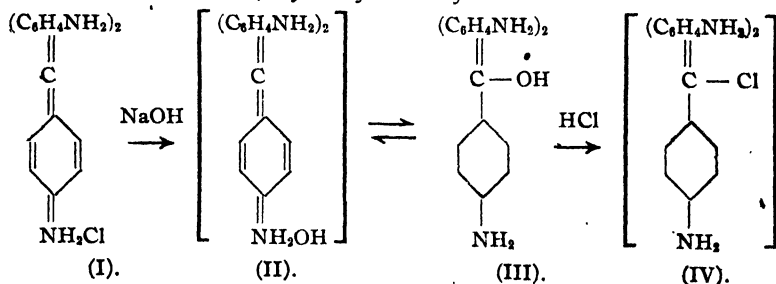
### I. Introduction.

**Historical.**—The historical development of the application of the tautomeric hypothesis to the triphenylmethane derivatives may be said to fall mainly within the following periods:

(1) The complex dyes were considered as possessing of necessity a radically different constitution from that of the corresponding triaryl-carbinols, for the very reason of the striking difference in properties. The dyes were *assumed* to possess a quinonoid constitution (I) in contradistinction from the benzenoid constitution of the carbinols (III). The possible existence of compounds isomeric with the carbinols but themselves colored and quinonoid, or the existence of salts isomeric with the

dyes but colorless and benzenoid, was neither looked for nor suspected. The hypothesis of tautomerism had no consideration in the discussion of the constitution of the dyes.

(2) With the advent of the tautomeric hypothesis the constitution of the dyes became a subject of new interest. Hantzsch and his coworkers<sup>1</sup> have shown that crystal violet and other similar dyes, in solution, produce on addition of alkali, a colored, water-soluble base, which, like the original ammonium salt, is still dissociated to an appreciable extent and which only eventually changes over to the colorless, insoluble, non-dissociated carbinol. Hantzsch drew the conclusion that the water-soluble transitory compound possessing a marked electrical conductivity must be the true ammonium base. It, therefore, represents the labile desmotropic form (II), while the carbinol subsequently precipitating from the solution is the stable tautomer (III). In Hantzsch's nomenclature this evanescent ammonium hydroxide compound is the true base, while the stable carbinol is the *pseudo-base*. Henceforth the basic dyes of this series were considered merely as salts of the extremely unstable quinonoid colored ammonium base, the desmotropic colorless salts (IV) still remaining unknown. Similar considerations were extended to cover also the constitution of the acid, hydroxylated dyes.



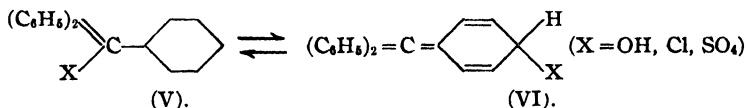
(3) It was realized that triphenylcarbinol itself, devoid of either basic or acid auxochrome groups, gives on combination with some acids, as halogen acids, colorless ester-like compounds of benzenoid constitution (V), as might normally be expected of tertiary alcohols; on combination, however, with other acids, as sulfuric acid, it was found that intensely colored compounds are produced possessing at the same time salt-like nature. Here again it was sought to explain this strikingly divergent behavior by assuming the presence of the chromophor quinonoid nucleus in the colored derivatives<sup>2</sup> (VI), *i. e.*, by considering these salt-like substances as the salts of the quinocarbonium base, which is, of course, the hypothetical desmotope of the carbinol itself. Although the quinonoid

<sup>1</sup> Hantzsch and Kalb, *Ber.*, **32**, 3109 (1899); Hantzsch and Ostwald, *Ibid.*, **33**, 278 (1900).

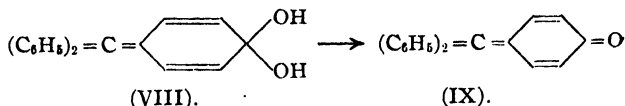
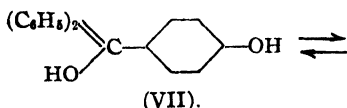
<sup>2</sup> Kehrmann, *Ber.*, **34**, 3815 (1901); Gomberg, *Ibid.*, **40**, 1847 (1909).



constitution of the sulfate received substantial corroboration of experimental nature, nonetheless there still lacked for the firm basis of the tautomeric conception in this group a single instance of the actual existence of a desmotropic pair of carbinols, one colored and the other colorless, or a single desmotropic pair of strictly isomeric derivatives, *i. e.*, two chlorides or two sulfates. Evidence of the possible existence of two forms of such derivatives was finally obtained in the case of the chlorides<sup>1</sup> themselves. When dissolved in liquid sulfur dioxide triarylcarbinols were found to give rise to colored solutions and to show a totally different chemical behavior from that when in any other solvent and when at the same time colorless. Their peculiar behavior when in this solvent was shown to be, by diverse experimental evidence, totally consistent with, and to be explainable only on the assumption that the colored modification possesses the quinoid constitution, and is in mobile equilibrium with the benzenoid modification. The isolation, however, of the colored halides in the solid state proved impossible, for on evaporation of the sulfur dioxide the equilibrium shifts wholly in favor of the benzenoid modification.



(4) The indisputable and direct evidence for the correctness of the tautomeric view was at last obtained in the shape of the two desmotropic forms of a carbinol. It has been found that parahydroxytriphenylcarbinol is capable of existing in both the colorless and the colored modifications.<sup>2</sup> The two forms were isolated in crystalline solid state and to these carbinols have been assigned the structures (VII) and (VIII).



Analogy alone should be sufficient to justify the structure assigned to the colored modification, analogy with the colored chlorides described in the preceding paragraph, and also analogy with the colored fuchsone, the constitution of which could only be as indicated (IX). But, further, it has been shown that there exists a striking difference in the rate of dehydration on moderate heating of the two carbinols. The ease with which the colored modification, in contradistinction to the colorless carbinol, changes

<sup>1</sup> Gomberg, *Ber.*, **40**, 1846 (1907); *Ibid.*, **42**, 406 (1909).

<sup>2</sup> Gomberg, *THIS JOURNAL*, **35**, 1035 (1913).

through loss of water into fuchsone is compatible only with a quinonoid structure for the former, wherein the two hydroxyl groups are linked to one and the same carbon atom.

(5) The fifth and final period in the development of the tautomeric conception as applied to the triarylmethane derivatives remains still unattained. It has not as yet proven possible to prepare two desmotropic chlorides in solid crystalline state, or two sulfates. As a near approach to the realization of this may be considered the fact that while the triarylcarbinol chlorides are colorless, another set of analogous acid derivatives, the sulfates, are always colored. A still nearer approach to this realization are some of the results described in connection with the study of the arylxanthenols.<sup>1</sup> It has been shown that while some arylxanthenol chlorides are colorless, others although entirely analogous, are colored; and again, with the same xanthenol the chloride may be colorless while the bromide is colored. But, in the dyes, there still remains unattained the isolation of the true ammonium bases tautomeric with the colorless carbinols, or of the colorless salts tautomeric with the dyes themselves.

**Object of this Investigation.**—A single carbinol has been reported as existing in two desmotropic forms and it seemed desirable to extend this study to the various substituted triphenylcarbinols, having in view the effects on the tautomeric tendency which might be brought about by various groups in the benzene ring. Since the greatest effect would probably be brought about through substitution in the same ring containing the parahydroxyl group, we have for the present studied the carbinols substituted in this ring, namely, those positions ortho to the hydroxyl group. It has been found possible to extend the instances of isolation of the desmotropic forms through a number of substituted carbinols, and at the same time to gain some knowledge what groups enhance or diminish the specific influence of the para hydroxyl groups. Whether of the simple groups only the hydroxyl, and only in the para position, has this specific influence, is difficult to say at present, and this must be left open for further study.

## II. Substituted *p*-Hydroxytriphenylcarbinols.

Gomberg and Jickling<sup>2</sup> have lately reported a new method for the preparation of *p*-hydroxytriphenylcarbinol by the condensation of benzophenone chloride and phenol. They formulate the reaction as passing through several successive steps in virtue of various intramolecular rearrangements and they have been able to isolate the intermediate products formed:

<sup>1</sup> Gomberg and West, *THIS JOURNAL*, 34, 1529 (1912).

<sup>2</sup> *THIS JOURNAL*, 37, 2575 (1915).

Diphenoxydiphenylmethane,  $(C_6H_5)_2C(OC_6H_5)_2$

*p*-Hydroxytriphenylcarbinol,  $(C_6H_5)_2C(OH)(C_6H_4OH)$

Di-*p*-hydroxytetraphenylmethane,  $(C_6H_5)_2C(C_6H_4OH)_2$ .

We have now studied the condensations of benzophenone chloride with other phenols and have found that this reaction offers a very general method for the synthesis of *p*-hydroxytriphenylcarbinols. We have prepared the carbinols required for our work by this method rather than to use the methods described for this purpose in the literature, which are laborious, involving many steps and giving only meager yields. We have studied the action between benzophenone chloride and the following phenols: *o*-cresol, guaiacol, *o*-bromophenol, *o*-chlorophenol, and *o*-nitrophenol. With the exception of the nitro compound, we have been able to show that a reaction analogous to the first step, as formulated by Gomberg and Jickling, takes place in every case without the aid of a catalytic agent. The various substituted diphenoxydiphenylmethanes have been isolated and are, generally speaking, similar in character and stability to the diphenyl ether of benzophenone. Likewise, the condensation with *o*-cresol, and with guaiacol, proceeded easily through the second step to the formation of the substitutes *p*-hydroxytriphenylcarbinols. With the monobromo- and monochlorophenols it was found that under similar conditions the reaction stopped with the first step, and only the substituted diphenoxydiphenylmethanes could be isolated. It was found that upon addition of the smallest amount of sulfuric acid the reaction between the chloro- or bromophenol and benzophenone chloride proceeded much more vigorously than when the reaction depended upon the hydrochloric acid generated during the course of the condensation. A satisfactory rearrangement of the chloro- and bromophenoxy compounds was only effected when, besides the addition of a drop of sulfuric acid, the reaction mixture was heated for twelve hours at  $110^\circ$ , but this unfortunately brought about decomposition products which made the isolation of the carbinols difficult. Much better results were obtained by substituting aluminum chloride for the sulfuric acid as the condensing agent. In the presence of anhydrous aluminum chloride, using carbon disulfide as a solvent, the reaction between the bromophenol or chlorophenol and benzophenone chloride yielded the desired carbinols, and for our further study this method was employed.

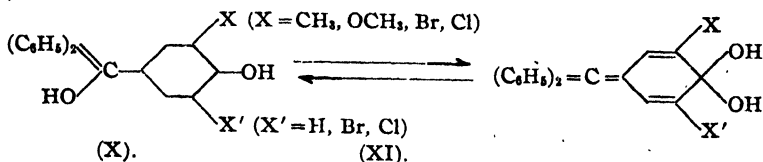
On long standing or when the reaction is carried on at elevated temperatures, benzophenone chloride and phenol yield a tetraphenylated derivative. Under similar conditions we have been able to carry the condensation between the benzophenone chloride and *o*-cresol or guaiacol to analogous compounds.

As previously mentioned, the reaction between *o*-nitrophenol and benzophenone chloride did not proceed in the desired manner. On mixing these

two substances together and slightly warming there was only the slightest evolution of hydrochloric acid gas; with the addition of a drop of sulfuric acid this was only slightly increased. By heating on the water bath there were signs of a more vigorous reaction, but the final product was a charred mass and nothing could be isolated from it. The use of aluminum chloride and carbon disulfide did not yield the desired results. Recourse was finally had by carrying on the reaction between benzophenone chloride and *o*-nitrophenol in the presence of anhydrous aluminum chloride without the use of a solvent, and from this reaction the nitro-substituted carbinol for our work was obtained.

By brominating and by chlorinating the cresyl and guaiacyl carbinols we obtained carbinols substituted in both positions ortho to the para-hydroxyl group, and these also were studied as regards their tendency toward tautomerization. Similarly, the monobromo- and monochloro-carbinols were further brominated and chlorinated, respectively, and the dihalogenated carbinols thus resulting were in their turn investigated.

**The Desmotropic Modifications of Substituted *p*-Hydroxytriphenylcarbinols.**—The substitution of various groups in the position ortho to the hydroxyl group did not materially change the general characteristics of the carbinols from those of the *p*-hydroxytriphenylcarbinol itself. In every case save that of the nitro compound we were able to isolate two distinct forms, the colorless benzenoid (X), and the colored quinonoid (XI).



The colorless variety is best obtained by first dissolving the carbinol in normal alkali, precipitating with carbon dioxide and finally crystallizing from such solvents as benzene, ether or alcohol. The second crop of crystals in some cases shows a slight tinge of color, indicating that without doubt the solution contains both forms in equilibrium, but with a predominance of the colorless modification.

The quinonoid modification is always obtained by crystallizing the benzenoid variety from 60 to 70% acetic acid, and in some cases it is necessary to heat the solution for a considerable time to effect a complete change. If recrystallization takes place from more dilute acid, 30 to 40%, the colored modification separates out with less color, higher melting point, and is doubtless a mixture of the two modifications. If stronger acid is used there results in some cases the fuchsone, in others a carbinol acetate. On repeated recrystallization of the quinonoid desmotrope, even without previous treatment with alkali, from benzene,

alcohol, or ether, there is a marked tendency to the formation of the benzenoid variety. The quinonoid carbinols in nearly all instances possess a lower melting point than the corresponding benzenoid modifications.

Although the transformations of the benzenoid modification into the quinonoid take place readily in solution, the identical changes may be brought about to some extent without the use of solvents. With the application of heat the white modification becomes colored, the melting point drops, and eventually, with the loss of a molecule of water, the fuchson is formed, the rapidity of these various changes being determined by the temperature chosen.

The effect of light energy will also bring about the change from the colorless to the colored modification and, although here the effect, to be sure, is much slower, nevertheless with sufficient time and by occasional stirring in order to expose all of the material to sunlight or light from a mercury lamp, a complete change may be effected.<sup>1</sup>

We have assigned, in each case, the benzenoid structure to the white modifications and to the colored carbinols the quinonoid formulation. The benzenoid structure for the colorless carbinols requires no further explanation, it being in harmony with the generally accepted view as regards this class of compounds. Our justification for the quinonoid structure rests upon the analogy to the triaryl halides in the colored form, the relation to the fuchson, and, particularly, *upon the rate of dehydration under the influence of heat as compared with that of the benzenoid modification*. We have carried out all the dehydrations at a temperature where the transformation from the benzenoid to the quinonoid modification is slow as compared to the loss of water from the colored compound, the temperature in each individual case being also so chosen as to minimize the possible decomposition of the resulting fuchson. In most cases a temperature of 75° proved the most favorable for our purpose.

### III. Reaction between Benzophenone Chloride and *o*-Cresol.

As has been said, the reaction between phenol and benzophenone chloride was found to take place in several successive steps. Between the reaction of phenol and *o*-cresol with benzophenone chloride there is no striking difference. Products which are similar to those isolated with the phenol reaction have been prepared in the course of this work through the reaction of benzophenone chloride upon *o*-cresol. Through the use of a solvent, from which the hydrochloric acid gas generated in the reaction between *o*-cresol and benzophenone chloride may be expelled either by boiling or by the rapid passage of dried air, we have been able to prepare the substituted diphenylether of benzophenone. Without the use

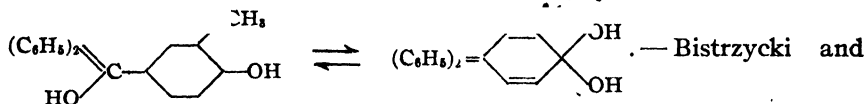
<sup>1</sup> Gomberg, *THIS JOURNAL*, 35, 1039 (1913).

of a solvent the condensation proceeds through the second step, yielding 3-methyl-4-hydroxytriphenylcarbinol, and even through the third step, giving 3,3'-methyl-4,4'-hydroxytetraphenylmethane.

**2,2'-Methyldiphenoxydiphenylmethane**,  $(C_6H_5)_2C(OC_6H_4CH_3)_2$ .—To the warm solution of 24 g. (1 mol) of benzophenone chloride in 250 cc. of dry benzene are added gradually 27 g. (2.5 mol) of redistilled *o*-cresol. The flask is fitted with a reflux condenser and protected from the moisture of the air by a calcium chloride tube. The solution is gently heated on the water bath, and when no further acid fumes are given off, usually after three to four hours, the reaction may be considered to be at an end. The benzene is evaporated off under reduced pressure and to the yellow oil remaining a few cc. of alcohol are added. Any excess of *o*-cresol or benzophenone chloride that may be present goes into solution in alcohol while the ether separates out as a white solid partly crystalline. For purification it is recrystallized from hot alcohol, and it then melts at 142°. The yield is nearly quantitative. The cresoxy compound is characterized by its insolubility in the ordinary solvents. It is stable to steam distillation, is not soluble nor decomposed by alkalis, but acids decompose it to benzophenone and the *o*-cresol.

Calc. for  $C_{27}H_{24}O_2$ : C, 85.21; H, 6.36. Found: C, 85.23, H, 6.47.

**3 - Methyl - 4 - hydroxytriphenylcarbinol** (*o*-Cresyldiphenylcarbinol),



Zurbruggen<sup>1</sup> first prepared *o*-cresyldiphenylcarbinol through the condensation of benzilic acid with *o*-cresol and subsequent removal of the carbon dioxide from the resulting cresyldiphenylacetic acid by use of especially prepared 100% sulfuric acid. The preparation by this method is laborious and the yields are comparatively small. On the other hand, according to our method, an almost theoretical yield of the cresyldiphenylcarbinol is obtained.

24 g. (1 mol) of benzophenone chloride are mixed with 27 g. (2.5 mol) of redistilled *o*-cresol, the mixture is at first cooled, and then allowed to stand at room temperature for from two to four days, protected from the moisture of the air by a calcium chloride tube. After the addition of a little water, the mixture is steam distilled to remove the excess cresol. The residue, after steam distillation, is digested with warm normal alkali and the solution, after cooling, is filtered from benzophenone not carried over in the steam distillation. To remove all traces of benzophenone which may be held in suspension or in solution by the alkali, the solution is shaken with small amounts of ether, and the ether dissolved in the

<sup>1</sup> *Ber.*, 36, 3558 (1903).

alkaline solution of the carbinol is removed from the solution by passage of a brisk stream of air. To the alkaline solution small amounts of solid sodium chloride are gradually added; on standing the sodium salt of the carbinol crystallizes out in long needles with almost no color. These are filtered, washed with a little water, redissolved in warm water, and the free carbinol is precipitated by passing carbon dioxide into the alkaline solution. On standing, the oily carbinol solidifies and is then filtered and air-dried.

Further purification of the carbinol is best accomplished by converting it into the insoluble acetate (see below) and then regenerating the carbinol. The crude carbinol is dissolved in a small amount of hot glacial acetic acid. On cooling and stirring the entire mass becomes suddenly solid, and the beautiful red crystals of the acetate thus formed may be filtered from the acid, while any tetraphenylmethane derivative that may possibly be present remains in solution in the acid. The red crystals of the carbinol acetate lose their acetic acid when allowed to stand exposed to the air. The resulting fuchsone is now hydrolyzed back to the carbinol by gently warming it with dilute alkalis and some alcohol or acetone, and is then reprecipitated from the solution with carbon dioxide. Further treatment of this carbinol is conditioned upon which of the two desmotropes it is desired to obtain.

**The Quinonoid and Benzenoid Desmotropes.**—On recrystallization of the purified carbinol from 60% acetic, the quinonoid modification of the carbinol is obtained pure, melting at 108–109° and colored a beautiful yellow. Bistrzycki and Zurbriggen reported that their carbinol melted at 108–109°, was yellow, and on recrystallization the melting point was raised. As a solvent they used acetic acid of 50% strength, and we have also found that with this strength acid the tendency to produce the colorless variety is only hindered by long heating. When the carbinol was precipitated from its alkaline solution by means of dilute acetic acid, Bistrzycki and Herbst<sup>1</sup> obtained a compound identical in composition with the original carbinol yet which, on recrystallization from benzene, was colorless and melted at 148–149°. We have been able to prepare this white variety of the carbinol, namely the benzenoid desmotope, by taking the product precipitated from alkaline solution by carbon dioxide and, after drying, recrystallizing it from alcohol, benzene, or ether and petroleum ether. In every case we were able to obtain a compound identical in composition to the colored carbinol, perfectly white and melting at 148–149°, although often the second batch of crystals showed signs of the colored modification. By dissolving the colorless modification in 60% acetic acid and warming for a short time, the colored carbinol, melting at 108–109°, is obtained. If acid of less strength is used the melting

<sup>1</sup> *Ber.*, 36, 3566 (1903).

point is lowered to 120–130° and the result is a mixture of the two desmotropes possessing a light yellow color. On the other hand, by repeated recrystallization from alcohol or benzene the colored carbinol gradually changes to the white, higher melting, benzenoid desmrope. On long exposure in a quartz dish to the rays of the sun, the white modification becomes yellow, but a similar change is noticed in the course of a few hours if the same compound is warmed to 60°.

Calc. for  $C_{26}H_{18}O_2$ : C, 82.72; H, 6.25. Found: Quinonoid desmrope, C, 82.56; H, 6.18; Benzenoid desmrope, C, 82.7; H, 6.24.

**Dehydration of the Two Forms of the *o*-Cresyldiphenylcarbinol.**—Equal amounts of the two desmotropes were heated at the same time in an especially constructed glycerol bath which allowed a very accurate control of the temperature. This bath consisted of a rectangular copper tank measuring  $9 \times 6 \times 4$  inches, through the entire length of which extended two copper tubes. When the bath was filled with glycerol and heated, by means of a Bunsen burner beneath, a thermometer which was immersed through an opening in the top into the glycerol showed less than a degree change of temperature during periods extending over several weeks. One gram of each desmrope was placed in a porcelain boat about five inches long, the boats placed each in one of the separate tubes, and a slow stream of carefully purified and dried air was passed throughout the period of heating. The rate of dehydration, *i. e.*, the loss of water, was carefully noted at different intervals. While the colored desmrope loses water rapidly, the white modification loses it slowly, *in proportion as it is being transformed under the influence of heat energy into the quinonoid desmrope*. In the tables below showing the rates of dehydration the time

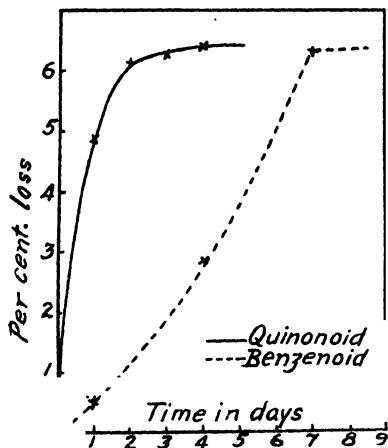


Fig. 1.

represents the different intervals of heating, while the percentages given show the total loss of weight in per cent. at the end of that interval. On longer heating the further loss in either case was on the average of 1 mg. per day, which, as will be shown, is due to the decomposition of the fuchson itself.

Temperature.	Time.	Quinonoid.	Benzenoid.
70°	24 hrs.	4.86%	0.47%
70°	24 hrs.	6.12%	1.31%
70°	24 hrs.	6.24%	1.81%
70°	24 hrs.	6.38%	2.85%
70°	70 hrs.	6.42%	6.30%

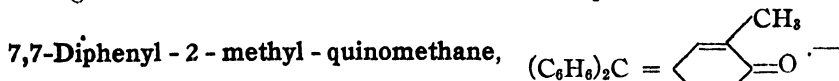
Calculated loss for one molecule of water is 6.25%.

**Decomposition of Fuchsones on Heating.**—When the dehydration of various carbinols was undertaken at temperatures ranging from 100°



to 150°, it was found that there resulted always a loss considerably more than that calculated for one molecule of water. We have been able to show that at temperatures from 75° and up appreciable decomposition of the fuchsone may take place with the production of small amounts of benzoquinone or its homologs, which are quite volatile, and the loss in weight, on heating the carbinols, in excess of that calculated for one molecule of water is thus accounted for. We have been able to isolate and completely identify benzoquinone resulting in this manner from *p*-hydroxytriphenylcarbinol; tolylquinone, from *o*-cresyldiphenylcarbinol; and methoxyquinone, from 2-methoxy-*p*-hydroxytriphenylcarbinol.

In view of this fact care has to be exercised to select for the dehydration experiments such a temperature that this decomposition would be a minimum, and our results justify the selection of 75°. The facts just described clear up a discrepancy in the observations made by Gomberg, on the one hand, and by Baeyer on the other. Gomberg<sup>1</sup> reported that by the action of silver sulfate on *p*-bromotriphenylchlormethane a *p*-quinone sulfate is produced and that this on hydrolysis yields fuchsone. The latter was not isolated at that time but its presence was inferred from several reasons, among them, by the distinct odor resembling that of benzoquinone. Baeyer<sup>2</sup> disputed the correctness of this observation claiming that the fuchsone has no odor. The fact that fuchsone on gentle heating does give rise to benzoquinone explains the discrepancy in the two observations. We have now verified that *freshly prepared fuchsone* is without odor, but when kept in a closed bottle, even if only at room temperature, in the course of several days it suffers sufficient autooxidation to give rise to an unmistakable trace of benzoquinone.



When either of the two modifications of the *o*-cresyldiphenylcarbinol are dehydrated, either by heat or by glacial acetic acid, there results the diphenyl-2-methylquinomethane. If the dehydration of the solid forms of the carbinol takes place at a low temperature, this transformation takes place without fusion of the material, and the resulting fuchsone melts at 173–175°. On recrystallization from benzene, it is obtained as deep red crystals melting at 176°, as described by Bistrzycki and Zurbruggen. It is very soluble in alcohol, ether or acetic acid.

Calc. for  $C_{20}H_{16}O$ : C, 88.19; H, 5.927. Found: C, 88.02; H, 5.935.

**Diphenyl-2-methylquinomethane Acetate.**—When either form of the carbinol is dissolved in hot glacial acetic acid and the solution afterwards cooled and stirred the entire mass becomes solid. The deep red crystals

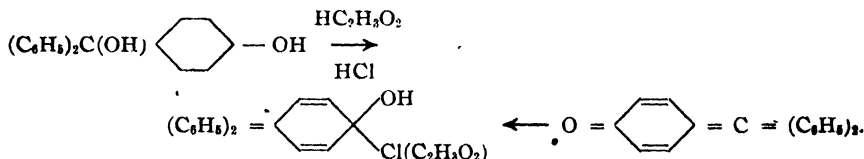
<sup>1</sup> *Ber.*, 40, 1853 (1907).

<sup>2</sup> *Ibid.*, 40, 3086 (1907).

resulting may be filtered off, washed with petroleum ether, dried between filter papers and used for analysis. The same product results if the carbinols are dissolved in the cold and the acid solution is allowed to stand, when the acetate resulting separates out, owing to its lesser solubility. On heating to  $75^{\circ}$  or on exposure to air the acetate loses the acid, leaving the fuchson. The loss in weight can be checked by passing the acid evolved into a standard alkali solution.

Calc. for  $C_{20}H_{16}O + C_2H_4O_2$ :  $C_2H_4O_2$ , 18.08. Found:  $C_2H_4O_2$ , 18.07, 18.13.

The influence of the *p*-hydroxyl group in inducing tautomerization of this cresyl carbinol to the quinoid state is well brought out by the existence of this colored acetate. Triphenylcarbinol itself also gives an acetate but that one is perfectly white. On the other hand, *p*-hydroxytriphenylcarbinol, when dissolved in sufficient cold glacial acetic acid to make a saturated solution, deposits on standing the acetate intensely colored. Still better results are obtained by starting with the cold saturated solution of the diphenylfuchson. The reaction in this case with acetic acid is not unlike that with hydrochloric acid.



**3,3'-Methyl-4,4'-hydroxytetraphenylmethane**,  $(C_6H_5)_2C(C_6H_3CH_3 \cdot OH)_2$ .—If the reaction mixture between benzophenone chloride and *o*-cresol is allowed to stand several weeks, or if the reaction is carried on at temperatures slightly elevated, the condensation goes to the final step and from the product that results one can isolate appreciable amounts of the substituted tetraphenylmethane.

To 14 g. of benzophenone chloride were added 16 g. of distilled cresol and the mixture was warmed on the water bath for three days. The reaction mixture was then steam distilled to remove the excess of cresol, taken up in normal alkali, the latter shaken with ether to remove the benzophenone, and the product thrown down by the addition of dilute acetic acid to the alkaline solution. On crystallization from dilute acetic acid, it separated out as white crystals melting at  $183^{\circ}$ , which, on recrystallization from benzene, alcohol, acetic acid or toluene, melt at  $190^{\circ}$ . Unlike di-*p*-hydroxytetraphenylmethane, this compound is extremely soluble.

Calc. for  $C_{28}H_{24}O_2$ : C, 85.22; H, 6.36. Found: C, 84.82; H, 6.56.

#### Attempts to Isolate the Free Radical.

**3-Methyl-*p*-carboethoxytriphenylcarbinol**,  $C_2H_5O.CO.OC_6H_3CH_3 \cdot (C_6H_5)_2COH$ .—As the carbinol chloride itself could not be expected to give the free radical the hydroxyl group was protected by the carboethoxy



cresylidphenylcarbinol takes place in either acetic acid or chloroform. For this purpose the carbinol was dissolved in glacial acetic acid and to this solution was added gradually a large excess of bromine dissolved in the same solvent. After standing at room temperature with occasional shaking, it was warmed on the water bath for a few hours. On cooling slowly there separated out deep red crystals. These were shown, by analysis, to contain bromine substituted in the benzene ring and removable only by drastic treatment, as fusion with sodium peroxide; also bromine which could be easily hydrolyzed off, and in addition bromine that could be titrated by sodium thiosulfate. There can be no doubt that this red compound is a perbromide of a quinonoid-carbinol bromide with apparently three atoms of perbromine, as shown by titration with thiosulfate. Often on cooling too rapidly there separated out along with the crystals of the perbromide a black oil, but this can be put back into solution on application of heat and additional acid.

To obtain the bromocresylcarbinol from this perbromide, two methods may be employed. The red crystals are boiled with a large amount of water; or the perbromide may be taken up in ether, washed with a strong solution of sodium bisulfite in order to remove the bromine, and, after drying the ether solution, the carbinol may be precipitated by addition of petroleum ether. The product resulting in either case is likely to contain a considerable amount of the brominated fuchson. It is, therefore, advisable to redissolve the whole in warm alkali in order to hydrolyze the fuchson, and the carbinol is then precipitated out by addition of dilute acid or by passing carbon dioxide into the solution. On recrystallization from acetic acid 60%, the carbinol is colored red and melts at 138–139°. It represents the quinonoid modification. As was shown to be the case with the *o*-cresylcarbinol, more dilute acid brings about some loss of color in the carbinol and a variable rise in melting point, owing to the formation of a mixture of the

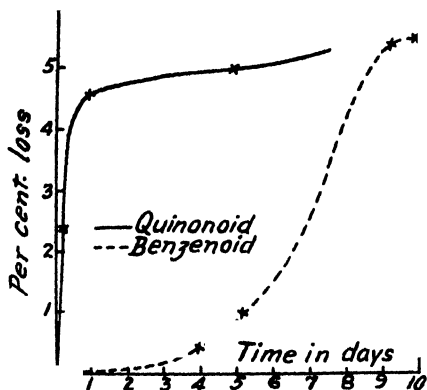


Fig. 2.

#### DEHYDRATION OF THE TWO MODIFICATIONS OF THE CARBINOLS.

Temperature.	Time of heating.	Quinonoid.	Benzenoid.
75°	3 hrs.	2.4	No loss
75°	22 hrs.	4.54	No loss
75°	24 hrs.	4.75	No loss
75°	24 hrs.	4.90	No loss
90°	48 hrs.	4.97	1.00
105°	120 hrs.	5.40	5.30
105°	48 hrs.	5.40	5.45

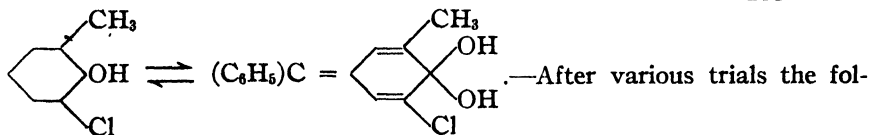
Calculated loss for one molecule of water is 4.89%.

To obtain the colorless desmotrope, the carbinol is dissolved in normal alkali, precipitated by means of carbon dioxide, and the product obtained filtered, dried, and recrystallized from benzene or ether and petroleum ether. On repeated recrystallization it is obtained entirely white and melts at  $145^{\circ}$ . The manner of the mutual transformation between these two modifications does not differ greatly from that observed and previously cited in the case of the *o*-cresylcarbinols. On the whole, however, the presence of the bromine in the nucleus imparts to the benzenoid desmotrope somewhat greater stability in the sense that it shows a lesser tendency to tautomerize to the quinonoid form than the non-brominated carbinol, and may be kept colorless for a longer time than the latter.

**Diphenyl-2-methyl-6-bromo-quinomethane**,  $(C_6H_5)_2C : C_6H_2BrCH_3 : O$ . —Dehydration of the carbinol in either desmotropic modification can be carried on at such a temperature that no fusion occurs and yet there results the brominated fuchsone compound. This, on recrystallization from benzene, is orange-red and melts at  $202^{\circ}$ . It dissolves in the ordinary organic solvents very easily but is insoluble in petroleum ether.

Calc. for  $C_{20}H_{18}OBr$ : Br, 22.72. Found: Br, 23.3.

**3 - Methyl - 5 - chloro - *p* - hydroxytriphenylcarbinol**,  $(C_6H_5)_2C(OH)CH_3$  —



lowing procedure was adopted for the chlorination of the *o*-cresylcarbinol: To 16 g. (1 mol) of cresyldiphenylcarbinol suspended in carbon tetrachloride was added chlorine (1 mol) previously dissolved also in carbon tetrachloride. As the reaction proceeds the suspended carbinol goes into solution with evolution of hydrochloric acid gas. Towards the end of the reaction the solution was warmed on the water bath, and then concentrated to a small bulk. On standing there separated out the chlorofuchsone, an orange-colored compound. To hydrolyze it to the carbinol, it was found necessary to warm the fuchsone for a long time with alkali. The carbinol was then precipitated from the alkaline solution by means of carbon dioxide, dried and recrystallized from 60% acetic acid. Unless heated for some time with acetic acid of this strength, quinoidation is likely to be incomplete. The quinonoid desmotrope thus obtained possesses a yellow color and melts at  $133^{\circ}$ . If recrystallization of the quinonoid carbinol takes place from alcohol, benzene or ether, the carbinol is partially changed into the colorless desmotrope. It is, however, difficult to obtain an entirely white compound

in this way except by repeated recrystallizations. If, however, the colored carbinol is first dissolved in normal alkali and then, after reprecipitation with carbon dioxide, is dissolved in any of the above-mentioned solvents, it appears as an entirely white compound, melting at  $149^{\circ}$ .

The white modification of the chlorocresylcarbinol shows a stability far greater than any of the colorless modifications so far mentioned. This stability shows itself in the dehydration experiment, the white carbinol changing but very slowly into the quinonoid carbinol under the influence of heat; furthermore, even on recrystallization from 60% acetic acid the colorless form persists in crystallizing out unless the solution is previously warmed for some time.

DEHYDRATION OF THE TWO MODIFICATIONS OF THE CARBINOL. TEMP.  $75^{\circ}$ .

Time of heating.	Quinonoid.	Benzenoid.	Time of heating.	Quinonoid.	Benzenoid.
$1\frac{1}{2}$ hrs.	0.71%	No loss	24 hrs.	5.6%	0.32%
4 hrs.	1.53%	No loss	48 hrs.	5.6%	0.62%
18 hrs.	3.1%	0.12%	72 hrs.	5.7%	1.72%
24 hrs.	4.3%	0.2%	after 12 days	5.7%	5.62%

Theoretical loss due to one molecule of water is 5.54%.

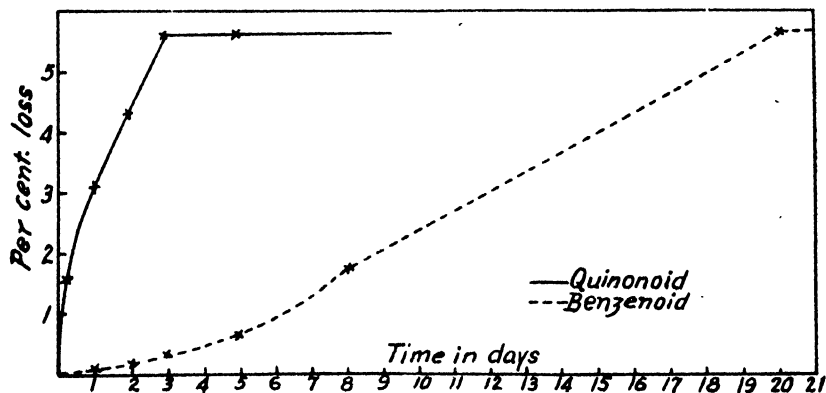


Fig. 3.

**Diphenyl-2-methyl-6-chloroquinomethane.**—This fuchstone, which results from the dehydration of either modification of the chlorocresylcarbinol, melts at  $197^{\circ}$  and is far more stable towards heat than most of the other analogs studied. It is easily soluble in most of the usual organic solvents. It is hydrolyzed with difficulty to the carbinol by alkali alone, but if a slight amount of alcohol is added to the alkali solution the carbinol is easily formed and passes into solution.

Calc. for  $C_{20}H_{18}OCl$ : Cl, 11.58. Found: Cl, 11.42.

#### IV. Reaction between Benzophenone Chloride and Guaiacol.

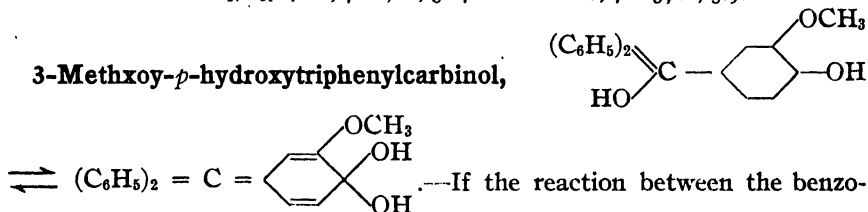
The reaction between benzophenone chloride and guaiacol follows the same course as the condensation of the keto-chloride with either

phenol or *o*-cresol. We have been able to so arrange the conditions as to obtain similar products to those isolated in these previously mentioned cases.

**2,2'-Methoxydiphenoxy-diphenylmethane**,  $(C_6H_5)_2C(OC_6H_4OCH_3)_2$ .—To the warmed solution of 24 g. (1 mol) of benzophenone chloride in benzene are added 30 g. (2.5 mol) of distilled guaiacol and the mixture heated on the water bath until the evolution of hydrochloric acid ceases. On evaporation of the excess of benzene a yellow oil separates out which on addition of small amounts of alcohol becomes solid and partly crystalline. This is filtered and recrystallized from hot alcohol or ether, in either of which it is only slightly soluble. When obtained in this manner it is a white compound melting at  $189^\circ$ . Like its analogs already mentioned, it stands steam distillation, is insoluble in alkalis, but acids decompose it into benzophenone and guaiacol.

Calc. for  $C_{27}H_{24}O_4$ : C, 78.6; H, 5.87. Found: C, 78.15; H, 5.90.

**3-Methoxy-*p*-hydroxytriphenylcarbinol**,



phenone chloride and guaiacol proceeds in absence of a solvent there results the substituted *p*-hydroxytriphenylcarbinol. This reaction takes place, however, much more slowly than in the case of phenol or *o*-cresol.

In a long-necked round-bottom flask 24 g. (1 mol) of benzophenone chloride are mixed with 30 g. (2.5 mol) of redistilled guaiacol and allowed to stand at room temperature for from two to three weeks. No attempt at cooling is necessary, since the reaction proceeds very slowly and apparently without generation of much heat. The manipulation for isolation of the carbinol differs but little from that employed in the isolation of the *o*-cresol carbinol. After steam distillation to remove the excess of guaiacol the product remains as a yellow oil which solidifies even while warm. This is digested with normal alkali, the solution is cooled and filtered, and the carbinol precipitated by means of carbon dioxide. On standing, this precipitate becomes solid and may be filtered, dried, and recrystallized from benzene. There is probably only the slightest trace of the tetraphenylated derivative present and this remains in solution while the triphenylcarbinol separates out from the hot benzene on slight cooling, being, unlike its analogs, but slightly soluble in this solvent. When obtained in this way the guaiacol compound is entirely white, and melts at  $159^\circ$ . It dissolves in 60% acetic acid with the production of color and after slight warming crystallizes out in the quinonoid modifica-

tion, melting at  $147^{\circ}$ , and is colored brown. The effects of heat, light, and solvents do not differ in general from those in the case of the carbinols

previously mentioned.

Calc. for  $C_{20}H_{18}O_4$ : C, 78.38%; H, 5.93%. Found (colored desmotrope): 77.92 and 5.72; (white desmotrope): 78.11 and 5.89.

#### DEHYDRATION OF THE TWO FORMS OF THE CARBINOL.

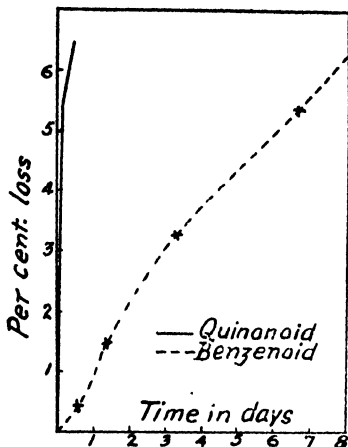


Fig. 4.

Temperature.	Time of heating.	Quinonoid.	Benzenoid.
$75^{\circ}$	15 min.	0.32%	No loss
$75^{\circ}$	15 min.	1.97%	No loss
$75^{\circ}$	30 min.	2.94%	0.10%
$75^{\circ}$	30 min.	3.94%	0.12%
$75^{\circ}$	45 min.	5.39%	0.15%
$75^{\circ}$	12 hrs.	....	0.39%
$75^{\circ}$	18 hrs.	....	1.46%
$75^{\circ}$	46 hrs.	....	3.27%
$75^{\circ}$	78 hrs.	....	5.37%

The loss calculated for 1 mol. of water is 5.24%.

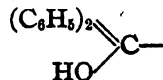
**Diphenyl-2-methoxy-quinomethane**,  $(C_6H_5)_2C : C_6H_3OCH_3 : O$ .—The fuchson which results from the dehydration of either form of the guaiacyl carbinol when recrystallized from benzene melts at  $183^{\circ}$ . It is very soluble in ordinary solvents, is with difficulty hydrolyzed to the carbinol by alkali, but more easily with the addition of slight amounts of alcohol. Of all the fuchsones studied we have found none of them as unstable towards heat as the guaiacyl fuchson. We have been able to isolate the methoxybenzoquinone which results from this decomposition and have found that its melting point is  $145^{\circ}$ , as reported recently by Moore,<sup>1</sup> and not  $140^{\circ}$ , as has appeared in the older literature.

**2,2'-Methoxydi-*p*-hydroxydiphenylmethane**,  $(C_6H_5)_2C(C_6H_3OCH_3OH)_2$ .—We have been able to obtain this compound in small amounts by carrying on the reaction between benzophenone chloride and guaiacol at elevated temperatures.

12 g. of benzophenone chloride and 15 g. of guaiacol were mixed and allowed to react for a week at a temperature of  $60^{\circ}$  to  $65^{\circ}$ . In working up the reaction mixture in the usual way, there is precipitated from the acetic acid solution on the addition of water small amounts of a high melting compound. It is characterized by its solubility in benzene which renders its separation from the corresponding triphenylcarbinol derivative very simple. On heating it softens at  $200^{\circ}$  and melts at  $208^{\circ}$ .

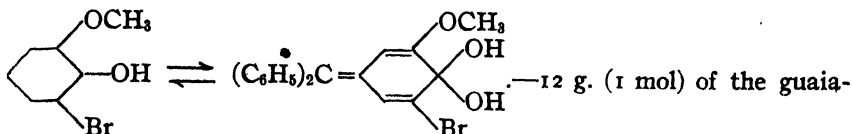
Calc. for  $C_{27}H_{24}O_4$ : C, 78.6; H, 5.87. Found: C, 78.73; H, 5.56.

**3 - Methoxy - 5 - bromo - *p* - hydroxytriphenylcarbinol**,



<sup>1</sup> *J. Chem. Soc.*, 99, 1045 (1911).





The reaction mixture is warmed on the water bath and finally concentrated to a small bulk. On cooling there separates out the brominated guaiacyl fuchson. The fuchson is hydrolyzed with normal alkali and the free carbinol is obtained in the benzenoid state by precipitation from the alkaline solution by means of carbon dioxide. On recrystallization from ether and petroleum ether it melts at  $156^{\circ}$  and is entirely white.

The quinonoid modification of the carbinol is obtained when the colorless carbinol is warmed with  $60^{\circ}$  acetic acid, and on crystallizing from this solvent it is an orange colored substance melting at  $151^{\circ}$ .

#### DEHYDRATION OF THE TWO MODIFICATIONS OF THE CARBINOL.

Temp.	Time.	Quinonoid.	Benzenoid.	Temp.	Time.	Quinonoid	Benzenoid.
$75^{\circ}$	14 hrs.	1.48	0.15	$75^{\circ}$	6 days	4.65	2.22
$75^{\circ}$	4 days	3.6	0.4	$95^{\circ}$	4 days	....	3.52
$75^{\circ}$	1 day	3.62	0.57	$95^{\circ}$	3 days	....	4.45
$75^{\circ}$	3 days	4.1	0.85	$95^{\circ}$	2 days	....	4.85

Theoretical loss for one molecule of water is 5.87%.

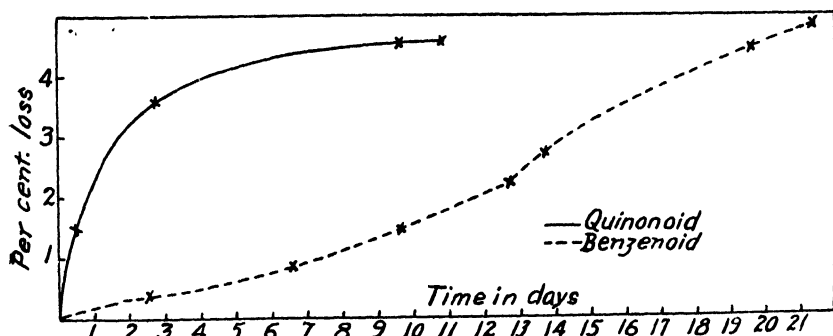
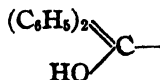


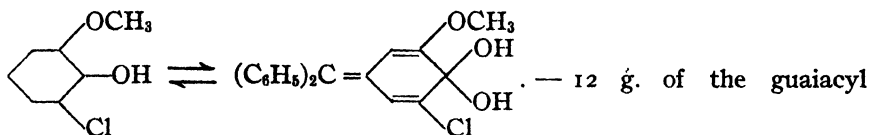
Fig. 5.

**Diphenyl-2-methoxy-6-bromoquinomethane.** — This bromoguaiacyl-fuchson is obtained by dehydration of either modification of the carbinol. It is stable at  $75^{\circ}$ , is soluble in benzene and acetic acid, and, when crystallized from either of these solvents, is a dark red compound, melting at  $232^{\circ}$ .

Calc. for  $C_{26}H_{18}O_2Br$ : Br, 21.77. Found: Br, 22.22.

3 - Methoxy - 5 - chloro - *p* - hydroxytriphenylcarbinol,





carbinol were suspended in a small amount of carbon tetrachloride and to this was gradually added the calculated amount (1 mol) of chlorine in solution in carbon tetrachloride. As the reaction proceeds the guaiacyl carbinol goes into solution and there is an evolution of hydrochloric acid gas. Towards the end of the reaction the mixture is warmed on the water bath. The carbon tetrachloride is evaporated and the fuchsonone thus obtained recrystallized from benzene. On long heating, this goes into solution in normal alkali and the chlorinated guaiacyl carbinol is obtained on reprecipitation by means of carbon dioxide. It is then recrystallized from 60% acetic acid, and the quinonoid modification is thus obtained. It is orange colored and melts at 159–161°. It dissolves in alcohol, benzene, or ether, the solution is only slightly colored, and on recrystallization from these solvents there is a marked rise in the melting point of the carbinol accompanied by loss of most of the color. The colorless modification is, however, best obtained by reprecipitation of the carbinol from its alkaline solution with carbon dioxide, and subsequent recrystallization from ether by addition of petroleum ether. When obtained in this manner, it melts at 166–168° and is perfectly white.

DEHYDRATION OF THE TWO MODIFICATIONS OF THE CARBINOL.

Temp.	Time.	Quinonoid.	Benzenoid.	Temp.	Time.	Quinonoid.	Benzenoid.
75°	9 hrs.	1.5%	0.101%	75°	96 hrs.	5.19%	1.90%
75°	42 hrs.	3.26%	0.496%	95°	220 hrs.	5.35%	4.90%
75°	70 hrs.	4.74%	1.09%	95°	48 hrs.	5.45%	5.21%

Theoretical loss calculated for one molecule of water is 5.26%.

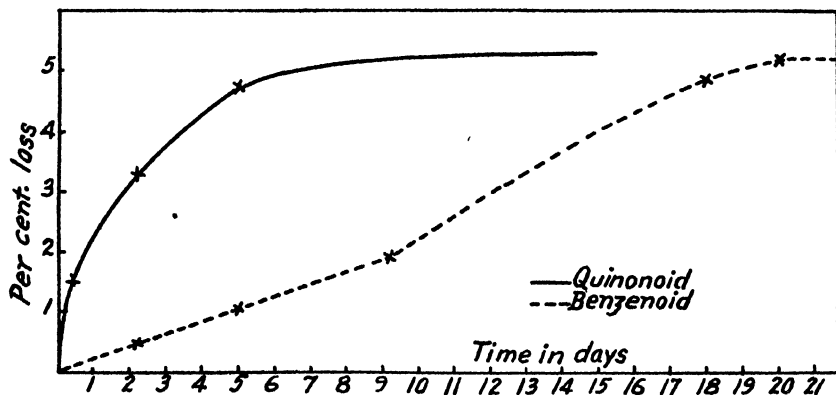


Fig. 6.

**Diphenyl-2-methoxy-6-chloroquinomethane.**—The chloroguaiacylfuchsonone results from the dehydration of either modification of the carbinol.

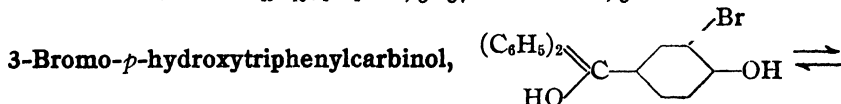
It remains unaffected when heated for a long period at  $75^{\circ}$ , is soluble in hot benzene, in both these respects differing from the unchlorinated guaiacyl fuchson. It melts at  $227^{\circ}$  and on hydrolysis with alkali yields the carbinol.

Calc. for  $C_{20}H_{18}O_2Cl$ : Cl, 10.98. Found: Cl, 11.01.

### V. Reaction between Benzophenone Chloride and *o*-Bromophenol.

**2,2'-Bromodiphenoxydiphenylmethane**,  $(C_6H_5)_2C(OC_6H_4Br)_2$ .—6 g. of benzophenone chloride were mixed with 7 g. of *o*-bromophenol, which had been prepared from *o*-amidophenol by Sandmeyer's reaction. The reaction mixture was allowed to stand at room temperature for several days, no cooling being necessary. During this interval hydrochloric acid was continually given off. The excess of bromophenol was steam distilled, the product digested with normal alkali, but no material soluble in alkali could be isolated, *i. e.*, the condensation under these conditions did not yield any triarylcarbinol. On cooling, the yellow oil solidified and it was found to consist mostly of benzophenone and some of the diphenoxyether, the two being separated from each other by the insolubility of the latter in alcohol. On recrystallization from hot alcohol the ether melts at  $184$ – $185^{\circ}$ . The theoretical yield of this same product may be obtained by carrying on the reaction between benzophenone chloride and *o*-bromophenol in benzene solution and at a temperature sufficient to expel all the hydrochloric acid formed in the reaction.

Calc. for  $C_{23}H_{18}O_2Br_2$ : Br, 31.37. Found: Br, 31.82.



$(C_6H_5)_2C = \text{Cyclohexane ring with Br and OH}$ .—The fact that the condensation of benzophenone chloride with *o*-bromophenol under the usual conditions, fails to proceed beyond the first step, led us to study more fully the means whereby the phenoxy derivatives may be transformed into the corresponding triphenylcarbinols. A series of experiments on diphenoxydiphenylmethane has shown that this ether gives rise to the carbinol not only under the influence of hydrochloric acid but also when heated in the presence of a very small amount of sulfuric acid. However, when applied to the bromophenoxyether, even this treatment failed to produce more than only a small amount of the carbinol accompanied by a large amount of decomposition products. Nor was the result improved by adding sulfuric acid to the mixture of benzophenone chloride and *o*-bromophenol.<sup>1</sup> We have finally been able to prepare the desired carbinol

<sup>1</sup> Sachs and Thonet, *Ber.*, 37, 3329 (1904).

by use of these same materials in the presence of anhydrous aluminum chloride in carbon disulfide solution at ordinary temperatures, thus avoiding the decomposition products obtained in the other case.

The procedure used was as follows: 24 g. (1 mol) of benzophenone chloride are dissolved in carbon disulfide and the containing flask surrounded by ice-water. Alternatively there are added small amounts of *o*-bromophenol and finely powdered aluminum chloride until 1.2 mols of each have been added. After the reaction has subsided the mixture is allowed to warm up to room temperature and finally warmed on the water bath. After the evolution of hydrochloric acid gas has ceased the product is cooled and decomposed in the usual manner. The product which separates out as a thick oil is then subjected to steam distillation in order to remove the excess of bromophenol and the product remaining digested with normal alkali. From the filtered solution the sodium salt of the carbinol is precipitated through the addition of solid sodium chloride. The sodium salt is filtered, washed with small amounts of water, redissolved in warm water and the carbinol precipitated by means of carbon dioxide. On standing, the precipitate becomes solid, and is then filtered, dried, and recrystallized from a small amount of carbon tetrachloride. The carbinol resulting is slightly yellow in color, melts at 107–109°, and is entirely white when further recrystallized from ether and petroleum ether. It then melts at 109°.

The colored modification is obtained when acetic acid 60% is used as a solvent. When recrystallized from this solvent, the carbinol is orange in color, and the melting point is 104.5–105°.

That the constitution of this carbinol is that of a *p*-hydroxy compound and not that of the isomeric *p*-bromocarbinol, the production of which is not at all excluded by the process of preparation which has been employed, is proven by the following: On brominating our monobromo compound we get a dibromo compound which is entirely identical with the diphenyl-3-5-dibromo-4-hydroxycarbinol, described by Auwers and Schröten,<sup>1</sup> and the constitution of which can be no other than as given below.

Calc. for  $C_{19}H_{15}O_2Br$ : Br, 22.51. Found: Br, 23.01.

**Dehydration of the Two Modifications of the Carbinol.**—Although there is but little variance in the melting points of the two modifications of the bromophenolcarbinols and although the transformation of the white compound to the colored modifications under the influence of heat takes place comparatively easily, yet the difference in rates of dehydration points unmistakably to a difference in structure.

<sup>1</sup> *Ber.*, 36, 3237 (1903).

Temperature 75°.

Time of heating.	Quinonoid.	Benzenoid.
6 hrs.	1.68%	0.43%
19 hrs.	2.95%	1.66%
7 hrs.	3.15%	1.76%
24 hrs.	4.26%	2.13%
13 hrs.	4.71%	2.51%
20 hrs.	5.03%	3.15%
12 hrs.	5.18%	3.43%
7 days	5.21%	5.01%

Calculated loss for one molecule of water is 5.07%.

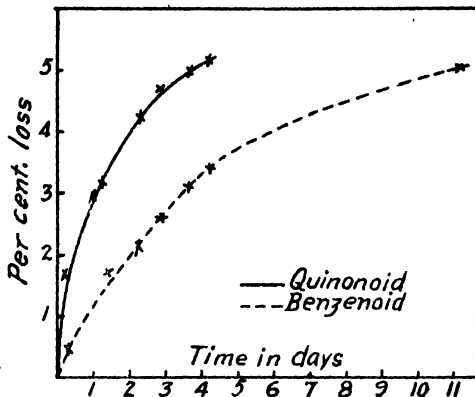
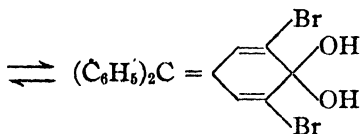
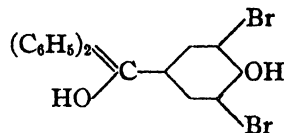


Fig. 7.

Diphenyl - 2 - bromoquinome -  
thane,  $(C_6H_5)_2C : C_6H_4Br : O$ . —

The product remaining from the dehydration of either form of the bromocarinol melts at 140° when recrystallized from benzene. This fuchsone is characterized by its low melting point, for all other fuchsones studied melt well over 160°.

3,5 - Dibromo - *p* - hydroxytriphenylcarbinol,



—This carbinol can be prepared, as has

been mentioned above, by brominating monobromo-*p*-hydroxytriphenylcarbinol. The more preferable method, however, is to brominate directly *p*-hydroxytriphenylcarbinol. The identity of the dibromides obtained by these two methods proves that the constitution assigned by us to the monobromocarinol as that of *p*-hydroxycarinol is correct.

Both Bistrzycki<sup>1</sup> and Auwers<sup>2</sup> have worked with the dibromocarinol, have recrystallized it from various solvents, but have failed to notice the existence of it in the two desmotropic forms.

The procedure for the purification of these compounds is as follows: *p*-Hydroxytriphenylcarbinol in acetic acid or in carbon tetrachloride is brominated with the required amount of bromine. The crude solid product is boiled with a small amount of glacial acetic acid. On cooling the insoluble dark orange-red dibromofuchsone crystallizes out, while any unbrominated carbinol remains in solution. The fuchsone is now hydrolyzed to the carbinol by gentle warming with dilute alkali and alcohol,

<sup>1</sup> Bistrzycki and Herbst, *Ber.*, 35, 3133 (1902).

<sup>2</sup> Auwers and Schröter, *Ibid.*, 36, 3237 (1903).

and the carbinol is precipitated by means of a stream of carbon dioxide or with very dilute acetic acid.

In order to obtain the benzenoid desmotrope the carbinol is recrystallized from benzene or from carbon tetrachloride, from which solvents it separated, however, with solvent of crystallization in each case. The crystals from benzene contain one-half molecule of solvent of crystallization, and this is held with considerable tenacity. Samples which have been kept in a desiccator for two weeks still contained about 8% of benzene, while the amount calculated for one-half molecule is 8.24%. The benzene, however, can be driven off at elevated temperatures, about 70°, but the carbinol acquires on this treatment a slight tinge of color. For our dehydration experiments, the carbinol freed from benzene was further recrystallized from ether and petroleum ether.

The preparation of the quinonoid desmotrope requires some care. The carbinol as obtained on the addition of dilute acid to its alkaline solution, is digested while still moist with 80% acetic acid, the filtered solution is gently warmed, and to it hot water is gradually added until the strength of the acid is reduced to about 60%. On cooling the quinonoid modification separates out in red crystals.

Although the two desmotropes differ strictly in their appearance, they both melt at about the same temperature. The purest benzenoid desmotrope melts at 138°, but in most instances the fusion point is found to be 134–136°, and this is the temperature at which the quinonoid modification melts. The colorless carbinol begins to turn quite red at about 90° and it is probable that the benzenoid desmotrope is almost completely converted into the quinonoid desmotrope before the fusion point is reached, and hence the identity of the melting points.

The two desmotropes may be differentiated from each other not only by their difference in color but also by their respective rates of dehydration on heating, as is the case with the pairs of tautomers of the other carbinols described in this paper. In the following experiment we employed, in obtaining the first set of curves, a sample of the benzenoid carbinol which has been obtained from its alkaline solution by treatment with carbon dioxide, washing thoroughly the precipitate and drying in a vacuum desiccator for two weeks. The quinonoid desmotrope employed was the crystalline compound ground to a powder in a mortar. Although the colorless compound was in a much finer state of division, yet the dehydration was slower than that of the colored. It is interesting to note the sudden breaks in the curves with the changes of temperature on heating. In the second experiment both desmotropes employed were crystalline and were reduced to about the same degree of fineness in a mortar and were kept at a constant temperature.

Experiment 1.				Experiment 2.			
Temp.	Time.	Quinonoid.	Benzenoid.	Temp.	Time.	Quinonoid.	Benzenoid.
90°	23 hrs.	1.69	0.47	85°	22 hrs.	0.84	0.18
90°	24 hrs.	2.21	1.01	85°	58 hrs.	2.3	1.06
100-5°	24 hrs.	3.24	2.42	85°	24 hrs.	2.52	1.50
90°	21 hrs.	3.61	3.06	85°	24 hrs.	2.70	1.80
100°	70 hrs.	3.84	3.72	85°	144 hrs.	3.60	3.52
100°	140 hrs.	3.91	3.81				

Calculated loss for one molecule of water was 4.1°.

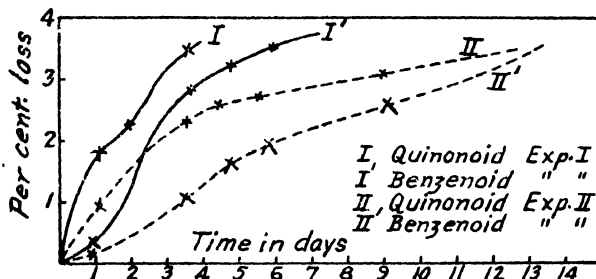


Fig. 8.

## VI. Reaction between Benzophenone Chloride and *o*-Chlorophenol.

In the reaction between *o*-chlorophenol and benzophenone chloride the same difficulties and limitations were encountered as in the condensation with bromophenol. The chlorinated phenoxy compound was readily produced, but we were unable to effect its rearrangement except under conditions which rendered the isolation of the triarylcarbinol difficult. Again, as with the bromophenol, we had recourse in the use of anhydrous aluminum chloride.

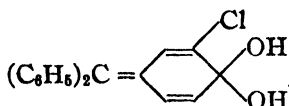
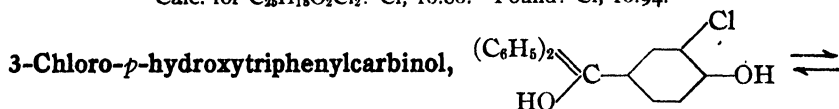
**Preparation of *o*-Chlorophenol.**—By direct chlorination of phenol there results mostly the *p*-chlorinated compound with relatively small amount of the *o*-chlorophenol. We have tried the various methods reported in the literature, and have found that the method reported by Lossen,<sup>1</sup> chlorinating in carbon tetrachloride solution by means of chlorine dissolved in this same solvent, yielded the best results, 100 g. of phenol yielding as much as 35 g. of the desired compound. For separation from the *p*-chlorophenol, as well as from the unchanged phenol, the method employed by Holleman<sup>2</sup> was used. The reaction mixture is suspended in potassium carbonate solution and shaken with ether, whereby the unchanged phenol is removed by the ether while the chlorophenols remain in the alkaline solution. This is now acidified, the liberated chlorophenols extracted with ether, the solution dried, and the phenols carefully fractionated.

<sup>1</sup> Friedlander's *Fortschritte*, 7, 89 (1903).

<sup>2</sup> Holleman and Rinkes, *Rec. trav. chim.*, 30, 79 (1911).

**2,2' - Chlorodiphenoxydiphenylmethane**,  $(C_6H_5)_2C(OC_6H_4Cl)_2$ . — The phenoxy compound could be isolated when the reaction between the benzophenone chloride and *o*-chlorophenol was carried out without the use of a solvent, but was more easily prepared, with theoretical yields, if the reaction took place in benzene solution warmed sufficiently to expel the hydrochloric acid gas given off in the reaction as soon as formed. On evaporation of the benzene and the addition of small amounts of alcohol, the chlorophenoxy compound separates out. On recrystallization from hot alcohol, it is obtained quite pure and it then melts at  $191-192^\circ$ .

Calc. for  $C_{26}H_{18}O_2Cl_2$ : Cl, 16.86. Found: Cl, 16.94.



— 12 g. of benzophenone chloride were dissolved in a small amount of carbon disulfide and the temperature of the solution kept down by means of ice-water. To this solution gradually and alternately small amounts of *o*-chlorophenol and aluminum chloride, finely powdered, were added until slightly more than one molecule of each had been used. The product is isolated in the same manner as the bromophenol compound, and it also is crystallized from carbon tetrachloride, from which it separates as a slightly colored material without a sharp melting point. On recrystallization from 60% acetic acid, the quinonoid desmotrope, deep orange and melting at  $118^\circ$ , is obtained. If the product obtained from the carbon tetrachloride solution is dissolved in alcohol, on standing there separates out the benzenoid desmotrope in large, transparent, colorless crystals, melting at  $70-72^\circ$ , with apparent loss of solvent of crystallization.

Calc. for  $C_{19}H_{15}O_2Cl + \frac{1}{2}C_2H_6O$ :  $\frac{1}{2}C_2H_6O$ , 6.9. Found:  $\frac{1}{2}C_2H_6O$ , 6.88.

If the alcohol of crystallization is driven off at a low temperature or by long exposure of the crystalline carbinol over calcium chloride, the product remaining is a white powder melting at  $126^\circ$ , and on recrystallization from benzene, or ether and petroleum ether, the melting point is not changed. Similar to the case with the analogous monobromocarbinol, the method employed for the preparation of the 3-chloro-*p*-hydroxytriphenylcarbinol did not exclude the possibilities of production of the isomeric 3-hydroxy-*p*-chlorocarbinol. That the carbinol prepared by the methods just given is nonetheless the *p*-hydroxy compound was definitely shown by further chlorinating the product obtained from this reaction. We obtained in this manner a dichlorocarbinol identical in every respect with the product obtained by direct chlorination of the *p*-hydroxytriphenylcarbinol, the constitution and properties of which are given later in this paper.



The transformation of the 3-chloro-*p*-hydroxytriphenylcarbinol from the white form to the colored modification takes place not quite as readily as with the corresponding bromocarbinol, as can be seen on comparison of the two sets of curves showing the relative values of dehydration.

TEMPERATURE 80°.		
Time of heating.	Quinonoid.	Benzenoid.
1 hr.	1.08	.....
16 hrs.	3.74	2.024
20 hrs.	4.98	2.376
40 hrs.	5.80	3.42
48 hrs.	....	4.35

Calculated loss for one molecule of water is 5.78%.

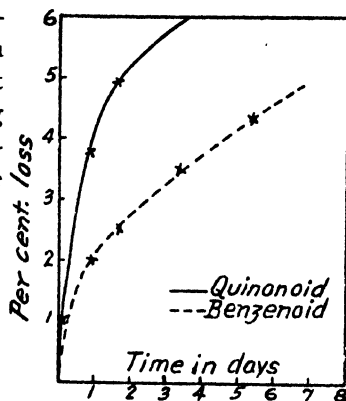
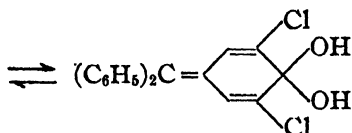
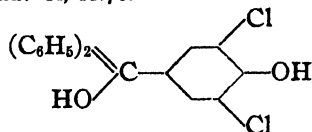


Fig. 9.

**Diphenyl-2-chloroquinomethane.**—The product remaining from the dehydration of either form of the chlorocarbinol consists of the chlorofuchson. It does not differ in properties from the bromofuchson, both of them showing remarkable stability over the guaiacylfuchson under the influence of heat. When crystallized from benzene it melts at 162–3°. On recrystallization from hot glacial acetic acid there separated out deep red crystals containing acetic acid, which is easily driven off at 75°. Here again, as in the instance of the *o*-cresylfuchson acetate, we are inclined to attribute to this compound the constitution of a quinocarbonium salt, namely, diphenyl-2-chloroquinomethane acetate.

Calc. for  $C_{11}H_{14}OCl$ : Cl, 11.42. Found: Cl, 11.70.

**3,5-Dichloro-*p*-hydroxytriphenylcarbinol,**



—This carbinol is best prepared from *p*-hy-

droxytriphenylcarbinol directly. The latter is suspended in carbon tetrachloride and to the cooled mixture a solution of chlorine in the same solvent is slowly added. The carbinol, on chlorination, goes into solution. The solvent is now evaporated and the residue is boiled up with glacial acetic acid. On cooling, dichlorofuchson, m. p. 217°, very little soluble in cold acetic acid, crystallizes out. The hydrolysis of the fuchson to the carbinol, further purification, and the isolation of the two desmotropes is carried out in the same manner as has been described under the 3,5-dibromocarbinol. The dichlorofuchson is darker red than the corresponding dibromo com-

pound, and the quinonoid carbinol possesses also a brighter red color than the dibromocarbinol. Here again, as has been found to be the case with the analogous dibromocarbinol, the benzenoid dichloro compound crystallizes from benzene and from carbon tetrachloride with solvent of crystallization. Furthermore, the two desmotropes cannot be differentiated from each other by their melting points, for both melt at approximately the same temperature,  $134^{\circ}$ . They can be differentiated, however, not merely by the difference in color but also by their respective rates of dehydration on heating.

### VII. Nitro-*p*-Hydroxytriphenylcarbinol.

The reaction between benzophenone chloride and *o*-nitrophenol was in no way similar to any other condensations previously studied. When mixed in the cold without the use of a solvent there was only slight action as judged from the amount of hydrochloric acid given off. Upon the addition of catalytic agents, a drop of sulfuric and addition of hydrochloric acid gas, this action was only slightly increased. At temperatures ranging from  $75$ – $100^{\circ}$  the evolution of gas was increased, but the resulting product was a charred mass from which nothing could be isolated. Recourse was had to methods similar to those employed with the *o*-bromo- and *o*-chlorophenols, but without satisfactory results, whether carbon disulfide or heptane (b. p.  $90^{\circ}$ ), was used. The condensation was finally brought about in the presence of aluminum chloride without the use of solvents, and resulted in the formation of the nitrohydroxycarbinol. 12 g. (1 mol) of benzophenone chloride and 7.5 g. (1.1 mol) of *o*-nitrophenol are mixed in a round-bottom flask and kept cool by surrounding with ice-water. To this mixture were gradually added 7 g. (1 mol) of anhydrous aluminum chloride. After the reaction is at an end, the mixture is heated on the water bath at  $60^{\circ}$ . Too high a temperature should be avoided; otherwise the result is a charred mass. After cooling, the aluminum salt is decomposed in the usual manner, the excess of nitrophenol removed by steam distillation, the product digested with normal alkali, precaution being taken to remove the benzophenone, and the sodium salt of the carbinol finally precipitated by addition of sodium chloride. The sodium salts already mentioned of the various carbinols were in every case white needle-like crystals. In the case of the nitrophenolcarbinol the sodium salt was bright red. The carbinol which results from the water solution of the sodium salt on the addition of acids is almost colorless. On recrystallization from 60% acetic acid, it does not change in color but always precipitates out with only a slight amount of color. It melts at  $97$ – $98^{\circ}$ . Recrystallization from any solvent does not change the melting point.

Calc. for  $C_{19}H_{15}O_4N$ : C, 71; H, 4.71; N, 4.36. Found: C, 70.68; H, 4.353; N, 4.273.

It is barely possible that here we have another instance of substituted triphenylparahydroxycarbinols occurring in but one modification, as is the case in certain carbinols studied in this laboratory by L. C. Johnson and which will be described later. The intense color of the sodium salt, in contradistinction from the carbinol itself, suggests the relation of acinitro to the true nitro compounds, so thoroughly studied by Hantzsch. The substance is now under further investigation.

### Summary.

1. It has been shown in this paper that benzophenone chloride condenses with various ortho-substituted phenols, in some instances requiring no catalytic agent, in others the use of aluminum chloride makes the yields more satisfactory. Under proper conditions this offers an excellent method for the preparation of various *p*-hydroxytriphenylcarbinols.

2. It has been shown that substitution of the groups, CH<sub>3</sub>, OCH<sub>3</sub>, Br, Cl in the ortho positions to the hydroxyl group does not deprive the carbinol of the tendency to tautomerize, and with each carbinol two desmotropic forms have been isolated. The various pairs of tautomers show remarkable similarity, as for example, in their melting points, in every instance the colored compound melting lower than the corresponding white desmotrope. Furthermore, the white higher melting compound, through heat or light energy, is invariably changed to the lower melting isomer.

3. Although as mentioned, the substitution did not hinder the tautomeric tendency in the carbinols studied, it resulted nevertheless in a gradation of this tendency. The various curves of dehydration, if placed on one diagram, would show clearly that at the temperature chosen, 75°, the various white desmotropes differ in their readiness to transform into the corresponding colored modifications, as judged by their rate of loss of water. For example, the monobromo-*p*-hydroxytriphenylcarbinol suffers transformation and subsequent dehydration in one-third the time as the chlorocresylcarbinol. Similarly, the colored modifications differ among themselves, as may be noted from the readiness of dehydration of the guaiacyl colored desmotrope as compared with the chloroguaiacyl colored compound under similar conditions. This, to be sure, does not indicate tautomeric tendency, but rather serves as a measure of the stability with which the two hydroxyl groups linked to one and the same *p*-quinone-carbon atom are held in the various quinoid carbinols, respectively.

4. The colored desmotropic modifications of the carbinols have been shown to possess the quinonoid constitution. The existence of so large a group of desmotropes removes the phenomenon of tautomerism in this series of compounds from the realm of chance, and offers a very strong support of experimental nature to the whole quinocarbonium theory

and to the quinonoid interpretation of the cause of color in the triphenylmethane series in general. This applies in no lesser degree to the free triarylmethyl radicals themselves. In the solid state they are nearly all colorless or only pale yellow, but when they are dissolved in some solvent, like benzene, intensely colored solutions result. We must assume from the evidence presented in this paper that the radicals dissolve with a simultaneous partial transformation to the quinonoid state.

ANN ARBOR, MICH

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY,  
No. 267.]

**RESEARCHES ON QUINAZOLINES. XXXIII. A NEW AND SENSITIVE INDICATOR FOR ACIDIMETRY AND ALKALIMETRY, AND FOR THE DETERMINATION OF HYDROGEN-ION CONCENTRATIONS BETWEEN THE LIMITS OF 6 AND 8 ON THE SORENSSEN SCALE.<sup>1</sup>**

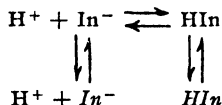
BY MARSTON TAYLOR BOGERT AND GEORGE SCATCHARD.<sup>2</sup>

Received June 19, 1916.

**Introductory.**

As a means of measuring hydrogen-ion concentration, the use of an indicator possesses the obvious advantage of convenience of operation, practically instantaneous readings and inexpensive apparatus.

Ostwald's explanation<sup>3</sup> of indicator action as due to an equilibrium between an ion of one color and an un-ionized molecule of another color (or colorless), has been quite generally abandoned in favor of the theory that an equilibrium exists between the two forms in both states.<sup>4</sup>



<sup>1</sup> Sørensen's system of expressing hydrogen-ion concentration has been used throughout, the "Index" ( $P_H$ ) being the negative common logarithm of the concentration of hydrogen ion, i. e., the negative exponent of the power to which 10 must be raised to express this concentration (Sørensen, *Compt. rend. Laboratoire de Carlsberg*, 8 (1909); Fales and Nelson, *THIS JOURNAL*, 37, 2771 (1915)). Thus, the index 6 represents a hydrogen-ion concentration of  $10^{-6}$ , and 8 of  $10^{-8}$ . This provides a single unit for expressing acidity and alkalinity, and one which can be measured directly by the use of the hydrogen electrode. Further, it is the relative and not the absolute change in hydrogen-ion concentration which affects both the electromotive force of the hydrogen electrode and the color of the indicator.

<sup>2</sup> The experimental work upon which this paper is based was carried out by Mr. George Scatchard in partial fulfilment of the requirements for the degree of Doctor of Philosophy under the Faculty of Pure Science of Columbia University.

Acknowledgments are also due to Dr. H. A. Fales, of this University, for much valuable assistance and advice.

<sup>3</sup> *Wissenschaftliche Grundlagen der analytischen Chemie*, 1901, 117.

<sup>4</sup> Stieglitz, *THIS JOURNAL*, 25, 1112 (1903); A. A. Noyes, *Ibid.*, 32, 816 (1910).

Yet, for a satisfactory indicator, just those conditions are necessary which approximate Ostwald's simple hypothesis so closely as to permit the application of the dilution law to them as to a simple dissociation. That is, for a two-color indicator, one tautomer must predominate in the ion and the other in the un-ionized molecule: while, for a one-color indicator, the colored form must be absent in one state. In either case, the equilibria between tautomers must be unaffected by external factors. With these conditions fulfilled, we may then ignore all but the predominating forms.

For a monobasic acid indicator ( $\text{In.H}$ ), the following relation will therefore hold:

$$(\text{H}^+) = K(\text{In.H})/\text{In}^-;$$

and for a monacid basic indicator ( $\text{In.OH}$ ),

$$(\text{H}^+) = K_w/(\text{OH}^-) = K_w(\text{In}^+)/K_B(\text{In.OH})$$

An indicator base may therefore be regarded as an acid with  $K_A = K_w/K_B$ .

We have omitted the term  $\gamma$  for the degree of ionization of the salt which Noyes uses in his equations, because its use assumes that the equilibrium between the tautomers in the un-ionized salt is the same as in the ion, and that the other ion which goes to make up the salt exists in the solution in the same concentration as the indicator ion. The second condition is seldom even approximately realized in practice, the first we do not know about. Since the error introduced by assuming  $\gamma = 1$  is small compared to that made by the other approximations, it does not seem worth while to use the very much more complicated form demanded by an exact expression.

For polybasic acids, or polyacid bases, the relations are more complex, but probably even then a single color change is affected by only one ionization, and the above relation holds at least approximately, which is all that is required for qualitative purposes.

By the depth of color of a one-color indicator, or the tint of a two-color one, the ratio of ionized to un-ionized indicator is measured, and thus the hydrogen-ion concentration. Although theoretically this ratio should vary with the change of hydrogen-ion concentration throughout the whole possible range, there is for every indicator a definite limited region within which this change of concentration is determinable by the color change. Outside this region either the small amount of one color is masked by the large amount of the other, in the case of two-color indicators; or, for one-color indicators, the amount of color is too minute to be visible, or too deep for the recognition of a slight change. The range of usefulness hence varies with the different indicators, but is usually one or two units of index. The location of this particular region of serviceability, depend-

ing as it does upon the ionization constants, naturally differs for different indicators. The location and extent of the serviceable range, and the accuracy of measurement, depend upon the amount of indicator required to give visible color. In general, one-color indicators have wider ranges than two-color ones, because of the masking of one color by preponderating amounts of the other, as already pointed out; and they give more accurate readings because it is easier to estimate depth of color than change of tint.

In titrations where the purpose in using an indicator is merely to determine when a certain definite concentration of hydrogen ion has been reached, the great advantage of a one-color indicator arises from the fact that the easiest of all color changes to detect is the first appearance of color in a colorless solution.

The accuracy of an indicator is impaired by any factors which cause a variation in the equilibrium between the tautomers. Certain substances affect the color change by disturbing the equilibrium without changing the concentration of hydrogen ion. Neutral salts affect most indicators and are particularly troublesome with those of the rosaniline series. Certain organic solvents, like alcohol, likewise often exert a disturbing influence.

Since the use of indicators for determining hydrogen-ion concentration is frequently resorted to in the case of biological liquids, the interfering factors in such solutions are of especial interest, notably the proteins and the commonly used preservatives. The effect of proteins is quite likely due to their colloidal nature, and becomes more serious as the molecular weight and complexity of the indicator increase, being most noticeable with azo indicators of Congo Red type. On the other hand, the disturbing action of the ordinary preservatives, such as chloroform and toluene, is usually due to extraction of the indicator, and those most seriously affected are the basic azo indicators.

Another factor to be reckoned with, is the color of the solution to be titrated. This difficulty may be partially remedied by giving the standard the same color, but it cannot be wholly overcome. For example, a yellow solution would impair but little the usefulness of phenolphthalein, but it would make trouble with methyl orange, and might preclude entirely the use of *p*-nitrophenol; the disturbance caused by a pink solution, on the other hand, would increase in just the opposite direction.

Still another matter of importance, is the permanence of an indicator color, particularly on standing exposed to ordinary daylight. Some indicators, like hematoxylin, run through a rapid series of color changes which make them unsuitable for measuring hydrogen-ion concentration; others fade on account of the precipitation of the indicator; practically all lose their color on long standing in strong daylight. This fading

may be so slow that the standards can be used for several days after they have been made up, or it may be so rapid that the indicator must be added at practically the same instant to the solutions which are to be compared.

For many titrations, an indicator must be used changing near a fixed point, because of the effect of the hydrolysis of the salt formed upon the hydrogen-ion concentration, and the common ion effect of the salt upon the acid or base. Except near this point, the change in hydrogen-ion concentration for a given amount of acid or base added is very slow; as is well illustrated by Hildebrandt's measurements, with a hydrogen electrode, of the hydrogen-ion concentrations at different points in certain titrations.<sup>1</sup> But, for the titration of a strong acid with a strong base; these influences are so slight that, with a proper correction for a blank on the water, the indicator may be selected throughout a wide range. In such cases, the delicacy is greatly increased when the end point is near the neutral point, because the color change depends upon the relative change in concentration, while the volume added affects the absolute change.

Assuming complete ionization, it requires 0.009 cc. of 0.01 molar monobasic acid to change the concentration of 100 cc. from an index of 7 to one of 6, while it requires ten times this amount to change it from 6 to 5, and 100 times to change it from 5 to 4. As the range of dinitrobenzoylene urea is from 6 to 8, it is appropriate to consider here other indicators available for this same change.

Azolitmin changes from red to blue with a change of hydrogen-ion concentration from 4.5 to 8.3; but the color change is too gradual for accurate work, and the indicator is useless in presence of protein.

*p*-Nitrophenol changes from colorless to greenish yellow from 5 to 7, and is but little affected by outside disturbing factors. Its chief objection is its color, which renders it unsuitable for use in artificial light or in yellow solutions.

Alizarin changes from yellow to red from 5.5 to 6.8. It is affected by protein and cannot be used in yellow solutions.

Neutral red changes from red to yellow from 6.8 to 8. It is affected by protein, chloroform or toluene.

Rosolic acid (commercial Coralline) changes from yellow to red from 6.8 to 8. The color change is poor and the indicator is affected by protein.

Cyanine changes from colorless to blue at 7 to 8, but is useless in presence of protein.

Hematoxylin and hematein give too rapid color changes.

Phenolsulfonephthalein changes from yellow to reddish violet from

<sup>1</sup> THIS JOURNAL, 35, 847 (1913).

6.50 to 8.50. The effect of salts and protein upon it is now being studied by Lubs and Clark.<sup>1</sup>

*o*-Cresolsulfonephthalein shows the same range and color change as the last, but its color change is less satisfactory. Lubs and Clark are studying the action of protein and salts upon it.

Bromothymolsulfonephthalein is also being studied by Lubs and Clark in the same way as to the effect of protein and salts. It shows a color change from 6 to 7.25 from yellow to blue.

So far as we are informed, there is no satisfactory indicator now known covering this range of 6 to 8. Sørensen says of this whole region, "il serait certes désirable de trouver des indicateurs supplémentaires."

The color change in the case of dinitrobenzoylene urea is from colorless to greenish yellow, the color developing regularly with the change in hydrogen-ion concentration from 6 to 8. This color change closely resembles that of *p*-nitrophenol, possesses the same advantage as a one-color indicator, and the same disadvantage due to its color being yellow. This is of interest, as the compound is structurally more closely allied to *p*-nitrophenol than to any of the other indicators cited, since it may also be regarded as of nitrophenol type. It is but slightly affected by neutral salts and not at all by chloroform or toluene.

Sørensen found that egg albumen was the most troublesome of all proteins with indicators, but that it did not affect *p*-nitrophenol. Comparative tests with egg albumen showed that dinitrobenzoylene urea is no more disturbed by it than is *p*-nitrophenol. The color of this new indicator fades but slowly. In phosphate solutions<sup>2</sup> it did not fade appreciably in two days, and but very slightly in a week.

Thus, it would appear preferable to rosolic acid (Coralline) for the preparation of neutral ammonium citrate solutions for fertilizer or soil analyses, since the hydrogen ion concentration of such solutions lies near the middle of its range, and it is possible to make much more accurate readings with it than with the older indicator.

In titrations, the acid side of the end point gave an index of 5.93 and the alkaline side 6.09, as measured by electromotive-force determinations with the apparatus described by Fales and Nelson.<sup>3</sup> These tests were made on phosphate solutions, as the reduction of the indicator by the hydrogen made it impossible to carry out these e. m. f. measurements in its presence, and because a buffer was necessary to keep the hydrogen-ion concentration constant. The figures recorded correspond to a change in hydrogen-ion concentration of  $3.6 \times 10^{-7}$ , or less than 0.004 cc. of

<sup>1</sup> *J. Wash. Acad. Sci.*, 5, 609 (1915).

<sup>2</sup> The primary and secondary alkaline phosphate solutions used throughout were prepared as described by Sørensen, *i. e.*, were  $1/15$  molar.

<sup>3</sup> THIS JOURNAL, 37, 2781 (1915).

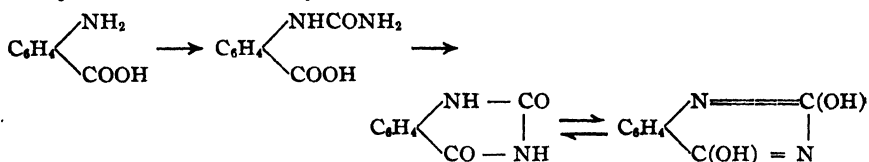


0.01 molar monoacid alkali to 100 cc. of solution (assuming ionization to be complete). In practice, the change was obtained with one drop of 0.01 molar NaOH. To give an equally distinct change under similar conditions requires in the case of *p*-nitrophenol 5-6 drops, and for methyl orange 10-12. Titrations of 0.01 molar HCl checked to within 0.1%.

This indicator can be used in hot or cold solutions, and its color is unaffected by nitrous acid. It gives a sharp end point with ammonium hydroxide solutions and hydrochloric acid. It can be used with NaOH and acetic acid, but it is impossible to titrate to the first yellow color. It cannot be employed to titrate carbonates, but the error due to small amounts of CO<sub>2</sub> is negligible.

It gives a second color change at 11 to 13, when the yellow color becomes much deeper, but this is too alkaline for most practical purposes. An attempt was made to use this color change for titrations of boric acid with NaOH, but it proved abortive, partly because the indicator gave a pale yellow color on the acid side of the end point, but principally because in such a strongly alkaline solution, a small change in index requires a large amount of alkali.

Dinitrobenzoyleneurea is readily prepared from anthranilic acid, by converting the latter first into the uramino (ureido) acid, which then easily condenses to benzoylene urea,



The benzoylene urea is nitrated with sulfuric and nitric acids, yielding a dinitro derivative, whose monosodium salt is used as the indicator. The location of the two nitro groups has not been definitely determined as yet, although one is quite certainly in position 6. The indicator action may be due solely to keto-enolic tautomerism, or the nitro groups also may play a part by pseudo-acid tautomerism themselves. In this connection, the second color change already noted at 11 to 13 is quite possibly due to the ionization of the second hydrogen.

The study of benzoylene urea and related compounds is being continued, and it is hoped that other serviceable indicators will come to light in the prosecution of the work.

### Experimental.

**Dinitrobenzoylene Urea**, C<sub>8</sub>H<sub>4</sub>O<sub>6</sub>N<sub>4</sub>.—20 g. anthranilic acid were dissolved in 700 cc. water and 15 cc. concentrated hydrochloric acid (calculated, 12 cc.) by warming. The solution was filtered, cooled, a solution of 15 g. KNCO (calculated, 12 g.) in 50 cc. water added slowly with mechanical stirring, this stirring being continued for 20 minutes after

all the  $\text{KNCO}$  solution had been added. The uraminobenzoic acid precipitated as a pasty white mass of microscopic needles. 300 g.  $\text{NaOH}$  were added with cooling. This dissolved the uramino acid and the sodium salt of benzoylene urea soon separated in crystalline form. After standing for four hours, the sodium salt was filtered out, dissolved in a liter of boiling water, precipitated with acetic acid, the free benzoylene urea filtered out, washed with water, and dried at  $120^\circ$ . Yield, 21.8 g., or 92%. The product formed colorless needles, m.  $353.4^\circ$  (corr.), which m. could not be raised by further crystallization.

10 g. of this benzoylene urea were heated on the water bath with 100 cc. concentrated sulfuric acid (which did not quite dissolve it all), and 12 cc. (calculated, 8 cc.) concentrated nitric acid (gr., 1.42) added. Heat was evolved, and the mixture turned bright red, but soon changed to bright yellow. After heating for an hour at  $100^\circ$ , the mixture was cooled and poured into a liter of ice and water, the precipitate filtered out, washed with water and recrystallized from a liter of 50% acetic acid. The crystals were removed, washed and dried at  $120^\circ$ . Yield, 14.4 g., or 92%.

Subs., 0.2026; 0.2786;  $\text{H}_2\text{O}$ , 0.0290, 0.0419;  $\text{CO}_2$ , 0.2846, 0.3895.

Calc. for  $\text{C}_8\text{H}_4\text{O}_4\text{N}_4$ : C, 38.08; H, 1.60. Found: C, 38.31, 38.13; H, 1.60, 1.68.

Subs., 0.1858, 0.1655; 36.60 cc. N at  $17^\circ$  and 765.4 mm.; 32.75 cc. N at  $20^\circ$  and 765.3 mm.

Calc. for  $\text{C}_8\text{H}_4\text{O}_4\text{N}_4$ : N, 22.19. Found: N, 22.28, 22.30.

As thus prepared, the compound formed pale greenish yellow prisms, decomposing at  $274.5^\circ$  (corr.), which decomposition point could not be altered by further recrystallization.

100 cc. of its aqueous solution saturated at  $23^\circ$  gave 0.0164 g. residue at  $110^\circ$  and 100 cc. of the water used gave 0.0007 g. residue. This solubility of 0.0157 g. per 100 cc. is equivalent to 0.00062 mols per liter, and corresponds to 14-15 drops of 0.01 molar indicator solution to 10 cc. of liquid to be tested.

The substance is very difficultly soluble in cold alcohol, or in ether, benzene, toluene, ligroin, chloroform, carbon tetrachloride or carbon disulfide; slightly soluble in acetone, ethyl acetate, cold acetic acid or boiling alcohol; moderately soluble in boiling water; readily soluble in boiling glacial acetic acid. It can be recrystallized from water or acetic acid. In solution of sodium hydroxide or carbonate, it dissolves with a yellow color, but is reprecipitated from such solutions by saturation with  $\text{CO}_2$ .

For the preparation of the sodium salt, 25 g. of the dinitrobenzoylene urea were dissolved in 115 cc. molar  $\text{NaOH}$  and 500 cc. boiling water, the solution filtered and cooled. A mass of long, bright yellow needles crystallized out. These were removed, pressed as dry as possible, and then left over concentrated sulfuric acid in an evacuated desiccator.

The rest of the dinitrobenzoylene urea was recovered by acidifying the filtrate. The sodium salt thus dried *in vacuo* was then heated to constant weight at 140–150°:

0.3195 g. subs. lost 0.0194 g.  $\text{H}_2\text{O}$ . Calc. for  $\text{C}_8\text{H}_5\text{O}_6\text{N}_4\text{Na}\cdot\text{H}_2\text{O}$ :  $\text{H}_2\text{O}$ , 6.17. Found:  $\text{H}_2\text{O}$ , 6.07.

Subs. (dried at 140–50°), 0.3001;  $\text{Na}_2\text{SO}_4$ , 0.0777. Calc. for  $\text{C}_8\text{H}_5\text{O}_6\text{N}_4\text{Na}$ : Na, 8.39. Found: Na, 8.38.

The solubility of the salt at 20° and at 2° was determined by taking a measured volume saturated at the desired temperature, heating to boiling, acidifying with hydrochloric acid, cooling, filtering out the precipitated dinitrobenzoylene urea, and drying to constant weight at 120° in a Gooch crucible. This gives the difference in solubility between the sodium salt and the free dinitrobenzoylene urea.

(1) 50 cc. solution saturated at 20° gave 0.4898 g. dinitrobenzoylene urea, indicating a solubility of 0.0389 mols per liter, or 1.1359 g.  $\text{C}_8\text{H}_5\text{O}_6\text{N}_4\text{Na}\cdot\text{H}_2\text{O}$  per 100 cc.

(2) 50 cc. solution saturated at 2° gave 0.1294 g. dinitrobenzoylene urea, indicating a solubility for the sodium salt of 0.0103 mols per liter, or 0.3008 g. per 100 cc.

In both the above calculations, the solubility of free dinitrobenzoylene urea at the temperature used has been assumed as zero. This, of course, is not strictly accurate, as the free dinitrobenzoylene urea is itself slightly soluble; but it is sufficient for all practical purposes, and those who wish closer figures can readily obtain them from the solubility results recorded above for the free dinitrobenzoylene urea.

The indicator solution was prepared by dissolving 0.292 g. of the salt in 100 cc. water, and was therefore 0.01 molar. The dropper used delivered 22–23 drops per cc. Fifteen drops of this indicator solution in 10 cc. 0.01 molar  $\text{HCl}$  gave no precipitate; 20 drops gave considerable. The solubility is thus about four times the amount ordinarily used in practice.

**Determination of Hydrogen-Ion Concentration.**—Phosphate and borate solutions were prepared as described by Sørensen. To 10 cc. of each, four drops of indicator solution were added. That with an index of 6 gave a colorless solution, while that with an index of 8 gave a distinct greenish yellow, the color developing evenly in the intermediate solutions.

Borate solutions with an index of 9 and 10 gave the same color as those with 8; 11 gave a slightly deeper color. 0.1 molar  $\text{NaOH}$  (index 13) gave a much deeper greenish yellow, one drop of the indicator giving as much color as four drops in a solution with index of 8.

**Effect of Toluene and of Chloroform.**—Phosphate solutions were prepared of index 6.4, 7.0 and 7.6. 30 cc. of each solution were made up, and each of these solutions then divided into three lots of 10 cc. each. These separate lots were then grouped into three sets of three lots each,

one of each index. One set was shaken with excess of toluene and filtered. Another set was given a similar treatment with chloroform. The third set was kept as a blank. Four drops of indicator were then added to each solution. No difference could be detected between the solutions of the same concentration in the three sets.

**Effect of Protein.**—25 cc. of egg white were diluted to 100 cc. with water, filtered, and 2 cc. of this solution added to a mixture of 14 cc. primary and 6 cc. secondary phosphate solution. This was then divided into two 10 cc. portions, to one of which *p*-nitrophenol was added and to the other the new indicator. Both showed an index of 6.60.

**Salt Effect.**—160 cc. secondary phosphate solution and 40 cc. primary phosphate solution were mixed and 12 g. NaCl (approximately molar) added. Electromotive-force measurements of this solution showed an index of 6.74, while the new indicator gave 6.90. Such a solution is more concentrated than any generally measured. The effect is apparently due to the large concentration of  $\text{Na}^+$  ion, which is responsible for the presence of un-ionized salt molecules which are colored like the ion.

**Fading Effect.**—Three sets each were made up of phosphate solutions of index 6.6 and of 7.6. Four drops of indicator were added to one set upon a certain day, to the second set on the second day, and to the third set on the third day. On this third day, no difference could be detected between the three sets of the same concentration. After standing for a week, the first set was compared with freshly prepared standards, with the following results: that with index of 7.6 had faded to 7.45–7.50, and that with index of 6.6 to 6.55–6.60.

**Titration.**—Titrations of 0.01 molar NaOH and HCl, using 10 drops indicator, gave 1.0011, 1.0004, 1.0009 and 1.0016, for the ratio of base to acid.

Titrations of 0.1 molar  $\text{NH}_4\text{OH}$  and HCl, using 10 drops indicator, gave 1.1257, 1.1262 and 1.1261, for the ration of acid to base.

Titrations of 0.1 molar acetic acid and NaOH, using five drops of indicator, gave 1.0129 and 1.0138, for the ratio of base to acid; but it was necessary to titrate by comparison with a color standard, instead of to the first appearance of a yellow color.

**Effect of Temperature on the End Point.**—Two 100 cc. samples of 0.005 molar NaCl (the approximate concentration at end point of titrations of 0.01 molar solutions) were heated to boiling and 10 drops of indicator added. One was titrated to one side of the end point, and the other to the other side. On cooling, no change was observed in the color in either case.

**Effect of Nitrous Acid.**—30 cc. molar HCl were diluted to 200 cc. (making it 0.15 molar), 1.5 g.  $\text{NaNO}_2$  (0.1 molar) added, and 40 drops of indicator (10 drops per 50 cc.). After standing for an hour at room

temperature, the solution was heated to 65° for a few minutes, cooled, and then titrated twice with 0.1 molar NaOH. A sharp end point was obtained in both cases, and the results checked closely, *viz.*, 1.0716 and 1.0715.

### Summary.

A dinitrobenzoylene urea has been discovered whose monosodium salt is a very sensitive indicator for hydrogen-ion concentrations between the limits of 6 and 8 on the Sørensen scale, changing from colorless to greenish yellow.

Structurally, and in its behavior as an indicator, it resembles *p*-nitrophenol more closely than any of the other well-known indicators. Like the latter, its chief disadvantage is its yellow color, which renders it unsuitable for work in artificial light.

It is but slightly affected by neutral salts, not at all by chloroform or toluene, proteins (egg albumen) have no more influence upon it than upon *p*-nitrophenol; its color fades very slightly in a week, and is unchanged by nitrous acid. It can be used in cold or in boiling (100°) solutions. It gives a sharp end point with  $\text{NH}_4\text{OH}$  and  $\text{HCl}$ , but cannot be used to titrate carbonates.

For the preparation of neutral ammonium citrate solutions, for fertilizer or soil analysis, it should prove superior to rosolic acid (commercial Coraline).

It can be prepared easily from anthranilic acid by the method described.

NEW YORK, N. Y.

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{CONTRIBUTION FROM THE LABORATORY OF PHYSIOLOGICAL CHEMISTRY OF THE UNIVERSITY OF ILLINOIS.}

## A COMPARATIVE STUDY OF THE DISTRIBUTION OF UREA IN THE BLOOD AND TISSUES OF CERTAIN VERTEBRATES WITH ESPECIAL REFERENCE TO THE HEN.

BY WALTER G. KARR AND HOWARD B. LEWIS.

Received June 5, 1916.

The problems of protein metabolism and protein requirements of the organism are today among the most absorbing and fundamental in the whole realm of physiological chemistry. Closely associated with these problems is the problem of the formation and distribution of urea, since this has long been recognized as the chief end-product of protein metabolism in the higher vertebrates, with the exception of birds and reptiles, in which its place as the chief end-product of nitrogenous metabolism is taken by the more complex uric acid. Although much work has been done on the relation of urea to the intermediary metabolism of protein and amino acids, many problems remain to be solved, the solution of which is now a possibility with the more suitable and accurate

methods of analysis developed in the last few years. The site of the formation of urea has not been determined, whether its synthesis be a function of the liver only, or one of all the tissues, nor is the significance of the variations of the urea content of the blood and tissues clearly defined. In view of this it has seemed of value to make a comparative study of the urea in the blood and tissues of several species of vertebrates, including also those animals whose main end-product of nitrogen metabolism is not urea.

Many of our recent developments in the knowledge of the rôle of urea in intermediary metabolism are due to the perfection of the methods for the determinations of small amounts of urea. Older methods were disadvantageous in that they required rather large amounts of blood, which necessitated experiments on large animals or the death of the animal to obtain sufficient blood for analysis. They were also inaccurate, as our present methods show us, in that either some of the urea was lost in the removal from the solution of interfering substances, or other substances were broken down and their decomposition products determined as urea. Of our present methods, those of Folin<sup>1</sup> and Benedict<sup>2</sup> have generally given satisfactory results in urine and other macro-analyses. But since they are known to break down the allantoin and a small part of the uric acid, creatinine, etc., quantities which are negligible in a macro-analysis, errors in the determination of small amounts are thereby introduced which render the methods of little value in tissue analysis. The most satisfactory method at present seems to be the urease method of Marshall<sup>3</sup> as modified by Van Slyke and Cullen.<sup>4</sup> The urease method is entirely specific for urea, also short and easy of operation, and with Folin's<sup>5</sup> aeration method for ammonia makes a very suitable and accurate determination of urea. Moreover, no removal of protein or other substance is necessary, thus avoiding loss in that respect.

On the distribution of urea in the animal organism many figures are available, but due to the inaccuracy of the older methods of determination, the figures of the last few years only would seem to be trustworthy. Schöndorff<sup>6</sup> reported a large number of figures on the urea content of tissues, but, due to the methods used, these are all apparently too high. He showed, however, that the distribution of urea was general in the body and the quantities approximately equal in different tissues, although his figures are not very consistent on this point. Marshall and Davis<sup>7</sup>

<sup>1</sup> *Z. physiol. Chem.*, **32**, 504 (1901); *J. Biol. Chem.*, **11**, 507 (1912).

<sup>2</sup> *J. Biol. Chem.*, **8**, 405.

<sup>3</sup> *Ibid.*, **14**, 283 (1913).

<sup>4</sup> *Ibid.*, **19**, 211 (1914).

<sup>5</sup> *Z. physiol. Chem.*, **37**, 161 (1902).

<sup>6</sup> *Pflüger's Arch. Physiol.*, **74**, 307 (1899).

<sup>7</sup> *J. Biol. Chem.*, **18**, 53 (1914).

have given an accurate method for urea analysis in tissues by means of the enzyme urease. They have shown that in the dog urea is distributed approximately equally in all the tissues of the organism with the exception of the fatty tissues, kidneys, and urinary tract, that the figures for normal dogs vary from 18 to 31 mg. urea per 100 cc. or g., and that on injection of urea into the blood stream it is absorbed very rapidly, only about 10% being left in the circulation at the end of the injection. They consider that the low content of urea in fatty tissues is due to the small percentage of water in these tissues and the subsequent decreased power of absorbing the urea, and that the high content of the kidneys and urinary tract is due to saturation with urea which is in the process of excretion from the body. Folín and Denis<sup>1</sup> published analyses of the urea content of the blood of different species, showing that it varies with the species. The same observers found the urea content of human blood quite constant at 11-13 mg. urea N per 100 cc. Schwartz and McGill<sup>2</sup> reported figures from fifteen different authors on the urea content of human blood showing a range from 11 to 25 mg. urea N per 100 cc. Cullen and Ellis<sup>3</sup> have shown that the urea concentrations of human blood and cerebrospinal fluid are practically the same under normal conditions. Denis<sup>4</sup> analyzed the blood of the elasmobranch fish (dog fish, sand shark, and skate) and found the urea content to be much higher than that of mammals (800-1000 mg. urea N per 100 cc. blood). The urea content of the blood of the teleosts (goosefish) on the contrary was lower than that of mammals, being about the same as that found by Folín and Denis<sup>5</sup> for chickens (8-9 mg. urea N per 100 cc. of blood). The urea content of the blood of other fish was about the same as that of mammals. Von Schröder<sup>6</sup> found 2.46-2.71% urea in the blood of sharks and somewhat less in the muscles and liver. Baglioni<sup>7</sup> suggests that this is very important, as the presence of urea in these animals is necessary for the life-processes of the heart and probably all the organs and tissues. No results of the comparative analysis of tissues by the new and accurate methods have been reported other than those of Marshall and Davis<sup>5</sup> on the dog.

In the present series of experiments we have analyzed the urea content of the blood and tissues of various species of vertebrates. The animals were placed under ether anesthesia, bled, and the blood collected in a vessel to which a small amount of potassium oxalate was added to prevent clotting. The tissues were removed, immediately placed in

<sup>1</sup> *J. Biol. Chem.*, **14**, 291 (1913).

<sup>2</sup> *Arch. Intern. Med.*, **17**, 42 (1916).

<sup>3</sup> *J. Biol. Chem.*, **20**, 511 (1915).

<sup>4</sup> *Ibid.*, **16**, 389 (1913).

<sup>5</sup> *Loc. cit.*

<sup>6</sup> *Z. Physiol. Chem.*, **14**, 576 (1890).

<sup>7</sup> *Centr. f. Physiol.*, **19**, 385.

weighed flasks containing ethyl alcohol and again weighed. The urea content was then determined by the method of Marshall and Davis.<sup>1</sup> The results are reported in Table I.

TABLE I.—THE UREA CONTENT OF THE BLOOD TISSUES OF VARIOUS SPECIES.  
Results Expressed in Mg. Urea per 100 g. of Tissue.

Species.	Blood whole serum.		Liver.	Heart.	Lungs.	Thigh.	Abdomen.	Breast.	Kidney.
Guinea pig 14	26	..	25	22	23	17	16	..	104
Guinea pig 7	26	..	26	23	27	19	31	..	50
Guinea pig 21	45	..	..	..	..	..	..	..	152
Guinea pig 16	52	..	..	..	..	..	..	..	...
Guinea pig A	43	42	..	..	..	..	..	..	...
Rabbit	60	60	65	38	40	32	..	..	155
Turtle 1	..	38	17	..	..	38	..	..	52
Turtle 2	28	..	..	..	..	..	..	..	...
Hen A	6	..	15	11	..	6	..	10	10
Hen 2F	9	..	16	8	..	9	..	10	...
Hen 2C	12	..	..	10	..	11	..	11	...
Hen 2D	6	..	..	5	..	11	..	11	...

The results of the analyses given in Table I show the variations of different species in the urea content of their blood and tissues. In agreement with the work of Bang<sup>2</sup> and Folin and Denis<sup>1</sup> there is considerable variation in the urea content between different species while individual variations of normal animals of the same species tend to fall within rather definite limits. The figures for the content of the blood and tissues of the guinea pig may vary from 25 to 50 mg. and the animal remain in an apparently normal condition. The data agree with those of Marshall and Davis<sup>1</sup> who showed that in the dog the urea was approximately equally distributed in all the tissues with the exception of the fatty tissues and the urinary tract. Thus in normal guinea pigs 7 and 14, the variations between tissues, except those of the urinary tract, were 16-31 mg. and 19-31 mg., respectively. On the other hand, the urea content of the kidneys, due presumably to contamination of the kidney tissue with urine was 104 and 50 mg., respectively. In these analyses and in others made in connection with a study of the influence of certain dietary factors on the urea concentration of the blood and tissues<sup>3</sup> we have observed wide variations in the urea content of the kidneys of guinea pigs maintained under similar experimental conditions (from 50 to 277 mg. per 100 g. tissue). We believe that these variations are to be attributed to differences in the concentration of the urine in the process of secretion at the time the animal was killed. The occurrence of considerable amounts of urea in turtle blood as a representative of the lower vertebrates is also

<sup>1</sup> *Loc. cit.*

<sup>2</sup> *Biochem. Z.*, 72, 104 (1915).

<sup>3</sup> Unpublished data from this laboratory.



of interest. In this connection it is worthy of note that urea has been found uniformly distributed in amounts varying from 20 to 30 mg. per 100 g. of tissue in the crayfish (*Cambarus virilis*).<sup>1</sup>

The results of the analysis of the blood of the hen are somewhat lower than those obtained by Folin<sup>2</sup> as he obtained 8 mg. urea N per 100 cc. These higher results may be due to the fact that he used a different method of analysis. In contrast to that of other animals the urea content of the tissues of the hen is low and that of the kidneys uniform with that of other tissues, which is in agreement with the fact that urea is not the end-product of nitrogenous metabolism in the hen. (Compare also Table II.) Analyses of the kidneys of hens for uric acid by the method of Benedict and Hitchcock<sup>3</sup> made in this laboratory have shown that the uric acid content of these organs is much greater than that of the other tissues as was to be anticipated from the composition of the hen's urine.

In order to determine the relation of urea to the intermediary nitrogenous metabolism in the avian organism, *e. g.*, hen, alanine was injected intramuscularly, the hens allowed to remain 2-5 hrs. and, after being placed under ether anesthesia, bled to death and the blood and tissues analyzed for urea. In one experiment urea was also similarly injected to show the distribution of urea following injection in the hen. The results are given in Table II.

TABLE II.—ANALYSES OF TISSUES OF HENS INJECTED WITH UREA AND ALANINE.  
Results Expressed in Mg. Urea per 100 g. Tissue.

No.	Amount injected.	Hrs. after injection.	Blood whole serum.		Liver.	Breast.	Thigh.	Heart.	Lungs.	Kidneys
C	2.5 g. alanine	2 hrs.	4	..	10	10	7	7	4	..
D	2.5 g. alanine	3 hrs.	4	..	13	9	8	..	..	7
E	2.5 g. alanine	5 hrs.	7	..	..	..	..	..	..	..
2E	2.5 g. alanine	3 hrs.	5 <sup>1</sup> / <sub>2</sub>	4	..	..	..	..	..	..
B	2 g. urea	2 hrs.	77	83	31	45	49	..	..	72
194 <sup>4</sup>										

The results show that when urea is injected into the animal it is transferred to all tissues of the body although apparently more slowly than in mammals.<sup>5</sup> When alanine is injected there is no increase in the urea content of the tissues. This would seem to indicate that urea is not an important intermediary product in the transformation of the amino acids to the final excretory product, uric acid, in the metabolic processes of the hen.

In Table I analyses of the blood of rabbit A, and in Table II of hens

<sup>1</sup> Jewell, unpublished results from this laboratory.

<sup>2</sup> *Loc. cit.*

<sup>3</sup> *J. Biol. Chem.*, 20, 629 (1915).

<sup>4</sup> Sample taken from the site of injection.

<sup>5</sup> Marshall and Davis, *Loc. cit.*

B and 2E, show that the distribution of urea is approximately equal between serum and corpuscles of the blood, which confirms the results found by Bang<sup>1</sup> and older investigators.

### Summary.

Values are given for the normal urea content of the blood and tissues of a number of species of vertebrates.

In vertebrates whose end-product of nitrogenous metabolism is urea, the kidneys are much higher in urea content than are the other tissues in which the urea content is about the same as that of the blood.

Hens injected with alanine do not show any increased amount of urea in the blood and tissues, indicating that urea is not one of the stages in the intermediary metabolism of amino acids in the hen. The kidneys of the hen have the same urea content as the other tissues, showing that urea is not present to any considerable extent in the kidney excretion of the hen.

URBANA, ILL.

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[CONTRIBUTION FROM THE LABORATORY OF THE NORTHWESTERN UNIVERSITY MEDICAL SCHOOL.]

## ON THE ASSUMED DESTRUCTION OF TRYPSIN BY PEPSIN AND ACID.<sup>2</sup>

BY J. H. LONG AND MARY HULL.

Received June 8, 1916.

This question is approached from two general standpoints. In one case it is a purely physiological one without reference to any therapeutic application whatever; in the second case the importance of the question comes from its bearing on the administration of ferments as remedies in disorders of digestion. Both points of view are interesting and important. In this laboratory the question comes up now as part of a problem dealing with the second point of view, and mainly through queries suggested by certain investigations prosecuted by the Council on Pharmacy and Chemistry of the American Medical Association, and particularly this question: What is the fate of the so-called pancreatins, administered by the mouth, in passing through the stomach? As digestive remedies have these preparations any real value? Do they, in any way, inhibit or diminish the activity of the pepsin in the stomach, or, on the other hand, are the components of the pancreas preparations themselves weakened or destroyed by the pepsin?

In part the queries suggested here are comparatively simple and easily

<sup>1</sup> *Biochem. Z.*, 72, 104 (1915).

<sup>2</sup> This investigation has been made with the assistance of a grant from the Committee on Therapeutic Research, Council on Pharmacy and Chemistry, American Medical Association.

answered. In several papers published from this laboratory<sup>1</sup> satisfactory answers have been given to some of the questions, and much of the older literature is quoted in them. But others of the points involved are evidently far from simple, although at first they would seem susceptible of easy solution. Their study involves the consideration of numerous subsidiary questions, some of which have not yet been fully answered. It is easy to arrange experiments *in vitro*, in which one group of ferments may appear to be readily destroyed by another, but it does not necessarily follow from these that under the conditions obtaining in the body a like result should be expected. In many of the published investigations the methods employed have been so narrowly limited as to fail to answer the last practical question, although doubtless giving correct conclusions for the arbitrarily chosen conditions of the experiment. For example, Mellanby and Woolley<sup>2</sup> in a recent publication have come to the conclusion that trypsin and steapsin are mutually antagonistic and that the latter is rapidly destroyed by the former. This may be true under some conditions, but scarcely under those which obtain practically. In our laboratory we have frequently made pancreatic extracts and mixtures in which both ferments exist and persist through a relatively long period. The stability and mutual action of ferments depend on a multiplicity of conditions which are properly balanced in the animal body, but which appear to present enormous difficulties in the duplication *in vitro*. Concordant and consistent results are, therefore, hard to secure.

In former work, and especially in the papers from this laboratory, referred to above, we believe sufficient evidence has been presented to show that the starch-converting ferment of the pancreas, the amylopsin, is so sensitive to the action of traces of acid and acid plus pepsin that its passage through the stomach must appear extremely doubtful under practical conditions. At the very beginning of the gastric digestion and before enough acid has been secreted to combine with the ingested proteins, amylopsin administered will doubtless persist and some of it may pass through into the duodenum. But with increasing hydrogen-ion concentration the conditions for its existence become less and less favorable.

It is not our intention to discuss in this place the behavior of amylopsin or steapsin, as the facts for the first seem to be pretty well established, while for the second many of the data necessary are as yet lacking. We shall confine our attention to the question of tryptic activity under a number of conditions with reference to peptic digestion.

In the papers quoted above<sup>3</sup> the fact is brought out that trypsin may

<sup>1</sup> Long and Johnson, *THIS JOURNAL*, 35, 897, 1188 (1913); Long and Muhleman, *Arch. Intern. Med.*, 13, 314 (1914).

<sup>2</sup> *J. Physiol.*, 48, 287 (1914).

<sup>3</sup> Long and Johnson, and Long and Muhleman, *Loc. cit.* The literature on this point is discussed.

be incubated with considerable quantities of hydrochloric acid without suffering appreciable loss of strength. In some of these cases of incubation through one-half hour the weight of acid was greatly in excess of the weight of the active tryptic ferment employed. These results have been secured so often and in solutions containing from 100 to 160 mg. of actual acid and 50 mg. of pancreas powder, containing trypsin and not trypsinogen, in 50 cc. of solution, that we are at a loss to understand the statements of Mellanby and Woolley<sup>1</sup> that, while trypsin withstands the action of weak acid pretty well, it is so quickly destroyed in acid of 0.2% strength that nothing can be said of the action of pepsin plus the acid on trypsin. In some of our experiments we have employed trypsin of more than the usual activity, but then the weights were so small that their protein content could not bind much of the acid.

These experiments showed, further, that the addition of pepsin to the acid worked a rapid destruction of the trypsin in some cases, while in others no such destruction was observed. The fate of the trypsin seemed to depend on the relation of the amount of protein present, and this practical point was left for further investigation. Meanwhile somewhat similar findings have been reported by Edie,<sup>2</sup> while Serono and Palozzi<sup>3</sup> reach the conclusion that pepsin and acid of 0.2% strength do not destroy the pancreatic enzymes. In Edie's experiments, in which Benger's ferment solutions were mostly employed, the behavior of small amounts of pepsin with large amounts of trypsin and fibrin in acid solution is studied. Under the conditions there can be no tryptic digestion, it is assumed, but a marked diminution in the extent of the peptic digestion was recognized. This cannot be attributed to any destructive action of the trypsin on pepsin, but the hypothesis is advanced that the trypsin exerts its effect by combining with specific groups of the protein complex in such manner as to prevent the pepsin from attacking them in the normal way. The practical bearings of the observations are somewhat remote because of the relative strengths of the solutions from which the results were obtained.

In investigating the action of pepsin on trypsin small volumes of solutions of the latter were allowed to act on much larger amounts of pepsin in presence of fibrin and sodium carbonate. Under these conditions there could be no peptic digestion of the fibrin, but the normal tryptic action appeared to be distinctly retarded. The same explanation is offered as in the other case. The pepsin is here assumed to combine with the protein in such manner as to protect the groups which the trypsin should attack. It will be seen that this is not quite the problem which

<sup>1</sup> *J. Physiol.*, **47**, 339 (1913-14).

<sup>2</sup> *Biochem. J.*, **8**, 84, 193 (1914).

<sup>3</sup> *Chem. Zentr.*, **84**, I, 1212 (1913); *Maly's Jahrb.*, **43**, 393 (1913).

we have on hand, since we wish to determine the action of pepsin on trypsin in acid solution. These investigations represent the physiological rather than the therapeutic side of the problem. Edie's work agrees fully with ours in showing the comparative stability of trypsin in presence of acid alone.

Serono and Palozzi appear to have worked with glycerol extracts of the pancreas, of their own preparation, obtained by aid of high pressure. These glycerol extracts when mixed with acid to make 0.2% strength could be incubated through 24 hrs. at the body temperature without losing their proteolytic activity. Nothing is said about the amount of protein present in the extracts which might serve as a protection to the trypsin by combining with the acid, but the impression is given that pepsin is practically without action on trypsin.

We have gone over these experiments at some length because they are the latest in the literature, and because, further, they leave the question not much nearer a solution than it was when opposite views were expressed by Ewald, Engesser, Mays and others' years ago. Ewald drew the conclusion from his experiments that trypsin is destroyed by digestion with pepsin and hydrochloric acid. But from the conditions under which his tests were made this result would of necessity follow without proving the point at all. For example, he incubated 700 mg. of pepsin and the same weight of trypsin, the Engesser preparation, with 100 cc. of 0.3% hydrochloric acid through three hours at 40°. As will appear below, destruction of trypsin would quite naturally result with these conditions. Engesser maintained that the preparation contained the "zymogen" rather than the finished trypsin, and for this reason should be very resistant. It appears, however, that he used relatively lower amounts of acid by his method of testing than did Ewald. Mays, noting the discrepancy between these results and the lack of agreement with earlier work of Kuehne on the behavior of trypsin, pointed out that the ferment is weakened or destroyed by acids, and that the rapidity of this destruction is hastened by presence of pepsin. He came to the conclusion, generally not admitted, that trypsin digests protein in acid solution when sufficient excess of protein is present, but overlooked the real condition under which trypsin appears to be stable when acid and pepsin are present. These three papers gave a basis for views which are often advanced, even down to the present time.

We have attacked the problem of the conditions of trypsin destruction in two ways. First by a series of experiments *in vitro* where a number of varying conditions with reference to strength of acid, amount and kind of protein present and resultant hydrogen-ion concentration were

<sup>1</sup> Ewald, *Z. klin. Med.*, 1, 615 (1879); Engesser, *Ibid.*, 2, 192 (1880); Mays, *Maly's Jahrb.*, 10, 298 (1880).

considered, and secondly through animal experiments on dogs with duodenal fistulas or Pawlow pouches, by aid of which the products of reactions might be withdrawn and tested. In a considerable number of cases the stomach contents have been withdrawn by a tube and examined as to the extent of the action. In this paper only the first group of experiments will be reported.

### **The Pepsin-Trypsin Reaction in Vitro.**

In these experiments the pepsin employed was an active commercial product which fully satisfied the requirement of the U. S. Pharmacopoeia, in the digestion of egg albumin. In the preliminary work we used the standard product of Fairchild Brothers and Foster and in the later tests the standard pepsin of Armour and Company. As tryptic preparations we have employed a variety of products. In much of our earlier work we used glycerol extracts of the pancreas of our own preparation. Some of these were freshly made and some had been on hand through long periods, to provide for a possible activation, which, however, did not seem to occur. We finally found it most convenient for comparisons to employ two brands of commercial trypsins from the laboratories of the firms whose pepsins we used. In most of the preliminary trials a product of Fairchild Brothers and Foster was used which had been in the laboratory some time and had lost part of its original activity. Later two other samples from the same firm were drawn in for comparison. In the larger number of routine tests the Armour and Company product was used in the digestions, and where convenient these digestions have been frequently carried out in presence of a phosphate mixture giving a hydrogen ion concentration of  $P_H = 7.7$ . But there are some drawbacks in the use of this buffer solution and the usual sodium carbonate medium found more frequent application. In each of the trial experiments of the short table below 3 g. of prepared moist, flake fibrin, yielding about 900 mg. of dry fibrin, was used in the substrate. This was mixed with 100 mg. of trypsin in 50 cc. of water, plus 50 cc. of approximately 0.4% sodium carbonate. The 100 cc. of mixture was protected by toluene in each case and incubated through 8 hrs. at 38°. Then a slight excess of hydrochloric acid was added and the liquids boiled to expel carbon dioxide. They were then made faintly alkaline to litmus and received an addition of 10 cc. of neutral formaldehyde. The final titrations with 0.2 *N* sodium hydroxide followed, with the results below. In each case a blank test was made with trypsin added from a boiled solution. The soluble nitrogen found in the blank test comes in part from the amino nitrogen of the ferments and in part from the effect of the long incubation. The hydrogen concentration at the end of the incubation was found to be essentially the same for all the mixtures, *viz.*,  $P_H = 8.1$ , which is a favorable concentration for activity.

TABLE I.—STRENGTH OF TRYPSINS.

Trypsin No.	1.	2.	3.	4.
NaOH required in actual test....	12.45 cc.	13.00 cc.	12.80 cc.	11.75 cc.
NaOH required in blank test....	3.90 cc.	3.80 cc.	3.70 cc.	3.80 cc.
	<hr/>	<hr/>	<hr/>	<hr/>
	8.55 cc.	9.20 cc.	9.10 cc.	7.95 cc.

In the next few tests, preliminary trials, trypsins 1, 2 and 3 were used; later, in the longer trials, trypsin 4.

It was to be expected that pepsin and trypsin preparations would furnish a certain amount of amino nitrogen in the digestions. The extent of this is suggested by the next tests, where the amount of the ferments used was the same as in the subsequent practical trials.

### Series A. Preliminary Tests.

#### *Pepsin and Trypsin without Additional Protein.*

In each of the following experiments 25 mg. of pepsin, 500 mg. of trypsin in 50 cc. of water and varying amounts of 0.1 *N* hydrochloric acid were made to a constant volume of 100 cc. and incubated through three hours at 38° in small flasks. The liquids were neutralized by the addition of the proper amount of sodium carbonate, well shaken to remove carbon dioxide, and then made up to 200 cc. in each case. These volumes were divided into two equal portions and one 100-cc. portion was boiled in each case to kill the ferments. To all the flasks enough sodium carbonate was added to make the hydrogen concentration the same, *viz.*,  $P_H = 8$ , as determined by preliminary trials. This required nearly 4 cc. of normal carbonate. The flasks were returned to the incubator and kept at 38° through 20 hrs., after which they were all made slightly acid to remove carbon dioxide on boiling, and brought back to litmus neutrality with 0.2 *N* alkali. In each case 10 cc. of neutralized formaldehyde were added and the usual titration made with 0.2 *N* NaOH. In the table below the results of the titrations are given, those with the unboiled trypsin being designated by A and those with the boiled trypsin by B.

TABLE II.—PEPSIN-TRYPSIN DIGESTION WITHOUT ADDED PROTEIN.

Vol. of 0.1 <i>N</i> HCl.....	50 cc.	40 cc.	30 cc.	25 cc.	22.5 cc.	20 cc.	15 cc.
A. cc. of 0.2 <i>N</i> NaOH.....	4.4	5.0	5.1	5.2	6.4	6.6	6.8
B. cc. of 0.2 <i>N</i> NaOH.....	4.4	4.2	4.2	4.2	3.8	3.8	4.3
	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
	0.0	0.8	0.9	1.0	2.6	2.8	2.5

It is evident that in the first few titrations the effect of the trypsin is practically negligible. The amino acid nitrogen from the peptic digestion and other causes is small and nearly constant, as shown by the blank titrations opposite B. However, when the amount of acid used at the start is below 25 cc. we seem to have a slightly larger weight of liberated amino acid nitrogen. This is possibly due to the self digestion of the

trypsin not destroyed in the acid digestion. The titration value in a flask containing 25 mg. of pepsin, 500 mg. of trypsin and 25 cc. of 0.2 *N* HCl and titrated without incubation was only 2.5 cc. of 0.2 *N* NaOH. It is important to note that the blanks from the action of the acid and pepsin alone are around 4 cc. always.

To test the effect of larger and increasing weights of pepsin in the digestion of fibrin with a constant weight of trypsin present the next series of digestions was carried out at 38°. In each case 3 g. of moist fibrin, equivalent to 0.9 g. of the dry substance, was taken with 500 mg. of trypsin in a volume of 100 cc. of 0.1 *N* HCl. Different weights of pepsin were added, as shown below. The mixtures were digested through three hours. Then enough carbonate was added to neutralize and leave an alkalinity of  $P_H = 8$ , after which a further incubation of three hours was carried out. The properly neutralized liquids were titrated with alkali after the formaldehyde addition in the usual way. The results are shown below.

TABLE III.—PEPSIN-TRYPSIN DIGESTION, WITH PROTEIN.

No.	Pepsin added.	Conditions varied.	Cc. of 0.2 <i>N</i> NaOH reqd
A.....	None	.....	5.5
B.....	50 mg.	.....	14.0
C.....	100 mg.	.....	15.0
D.....	100 mg.	3 hrs, acid digestion only	16.2
E.....	150 mg.	.....	14.5
F.....	150 mg.	both ferments killed	4.0

In A we have the effect of the preëxisting amino acid groups and possibly a slight digestion through the residual trypsin which may have survived the acid digestion in presence of the fibrin. In B and C we have a characteristic pepsin digestion. The flake fibrin disappeared completely so that the opalescent liquid could be easily titrated. In D there could have been no tryptic digestion as the incubation was stopped at the end of the three-hour acid period. The larger alkali volume used in titration has probably no significance. In E the conditions are the same as in B and C, but in view of the result in D it does not appear probable that we have any tryptic digestion here, and, therefore, not in B and C. F serves as a general control for the amount of amino nitrogen made soluble in the incubation alone, or as coming from the ferments themselves. This value subtracted from A leaves a remainder so small as to suggest that the assumed tryptic activity in the latter case must be practically negligible. It was pointed out above that trypsin survives a short acid digestion at this temperature very well, but it is evident that with or without pepsin present an incubation of three hours' duration in a medium containing 365 mg. of hydrochloric acid and 900 mg. of dry fibrin is sufficient to destroy the trypsin. This amount of dry fibrin can bind about 60 mg.



of the acid at the most, to the extent of rendering it inert as regards the ferment. Under tests B, C, D and E it is shown that the amount of amino nitrogen liberated by 150 mg. of pepsin from the given weight of fibrin is not essentially greater than the amount liberated by 50 mg. With the active pepsin used it is likely that the same result would be secured by even a much smaller weight of pepsin.

In the continuation of the preliminary experiments we employed smaller weights of pepsin and acid with the constant weight of 3 g. of moist fibrin and 500 mg. of trypsin in a total volume of 100 cc. Each mixture was incubated through 3 hrs. at 38°, the acid neutralized and the reaction brought to  $P_H = 8.1$  by sodium carbonate. At this point a further 3 g. of fibrin were added and the incubation continued through 20 hrs. at the same temperature. The contents of each flask was made slightly acid and boiled to drive out carbon dioxide, then brought to litmus neutrality, treated with 10 cc. of neutralized formaldehyde and finished in the usual manner. The results are shown in the table below. In half of the experiments the trypsin was killed by boiling in part of the water used for solution and these experiments are designated by the letters A', B', C' and so on.

TABLE IV.—PEPSIN-TRYPSIN DIGESTION WITH FIBRIN.

No.	Vol. 0.1N HCl. Cc.	Wt. of pepsin. Mg.	Vol. of 0.2N NaOH. Cc.	A—A', B—B', C—C', etc. Cc.
A.....	50	25	25.3	
A'.....	50	25	17.4	7.9
B.....	30	25	26.8	
B'.....	30	25	16.8	10.0
C.....	25	25	29.3	
C'.....	25	25	16.2	13.1
D.....	20	25	28.6	
D'.....	20	25	14.3	14.3
E.....	15	25	36.5	
E'.....	15	25	13.5	23.0
F.....	00	00	39.1	
F'.....	00	00	7.5	31.6

Tests F and F' at the bottom of the table are straight trypsin digestions carried out through the 20-hr. period only, in the weak alkaline medium, with the ferment in F' killed at the outset. In A', B', C', D' and E' we have peptic digestions in presence of diminishing amounts of acid. In all the peptic digestions where not less than 25 cc. of acid had been used the fibrin solution was practically complete in the three hours, and in the second, or alkaline digestion, in cases where not over 20 cc. of the acid had been used in the first digestion, the solution went so far that no neutralization precipitate formed when the excess of carbonate was finally destroyed by acid. In all cases the formaldehyde titration was made on the filtered liquid, with exclusion of the neutralization precipitate.

It is seen that in test F' of the table we have a blank of 7.5 cc. of 0.2 N alkali, and following an incubation in which the pepsin was omitted and the trypsin killed. This is larger than was found in Table III, No. F, where a blank of 4 cc. of the alkali is given. The trypsin weights were the same in the two cases. The conditions are not the same, however, since in Table IV we have a 20-hr. digestion period against 6 hrs. for Table III. Some greater solution may follow the longer digestion, and it is, of course, possible that in Table IV the trypsin had not been completely destroyed by the preliminary boiling. It has been pointed out that the resisting power toward heat is greater than was formerly assumed.

Aside from this slight discrepancy it is evident that a tryptic action is present in some of the mixtures of Table IV. With the larger weights of acid employed the peptic activity is marked, and that is shown in A and A', where the difference between the results of the two titrations is not large. The total protein is not sufficient to bind all the acid, and we have in consequence destruction of most of the trypsin. In the following tests, with diminishing weights of acid, the peptic digestions become gradually less, as shown by B', C', D' and E', while the combined digestions are correspondingly increased. The trypsin appears to be less and less injured until we have in E a very marked action, approximating the straight tryptic digestion shown in F. The acid of E is not sufficient to bring about a marked peptic digestion on the one hand, or to weaken the trypsin on the other.

#### Series B. Fibrin Digestion.

The experiments just discussed show beyond question that trypsin is able to withstand the action of pepsin and hydrochloric acid under some conditions, while under other conditions there is, apparently, a destruction of the trypsin in acid solution. More detailed experiments are necessary to bring out the facts, and these follow. Fibrin was used for some of these later experiments, but casein and meat, both raw and cooked, have also been used. In what follows a weaker trypsin was employed.

The general method of experimentation was essentially the same as described above, with this modification. After incubating the mixture of 25 mg. of pepsin, 500 mg. of trypsin, protein and acid, made up to 100 cc., through a period of three hours, and neutralizing then exactly with sodium carbonate, the liquid was made up to 200 cc. This volume was divided into two equal portions, one of which was boiled to kill any trypsin left. Both portions were brought to a  $P_H$  concentration of approximately 8.1 with carbonate and each received an addition of 3 g. of moist fibrin. All the flasks holding the mixtures of the series were incubated through 20 hrs. at 38°, made then slightly acid with hydrochloric acid, boiled to remove carbon dioxide and throw out any neutralization precipitate and the contents filtered. The filtrates were brought to litmus neutrality,

treated with formaldehyde and titrated with 0.2 *N* NaOH in the usual manner.

In these experiments, as distinguished from those of Table IV, there was only one flask incubated for each acid concentration, and in the division for the tryptic digestion in a 100 cc. volume the trypsin concentration would be just half what it was in the earlier experiments, for the new amount of fibrin added. A wider range of acid concentrations in the preliminary digestion was further chosen. In the tables below the results for the unboiled half of the incubated liquid are shown by A, B, etc., while the boiled portions are designated by A', B', etc.

The preliminary acid digestion mixtures contain, in the stronger concentrations, enough acid to saturate the protein, while in the lower concentrations this is not the case. The actual  $P_H$  values for several mixtures, from which others may be interpolated, are given below. The measurements were made at the end of the three-hour digestion period.

Vol. of 0.1 <i>N</i> HCl in 100 cc.	$P_H$ .	$C_H$ .	Vol. of 0.1 <i>N</i> HCl in 100 cc.	$P_H$ .	$C_H$ .
50 cc.	1.81	0.01550	25 cc.	2.58	0.00263
35 cc.	2.24	0.00575	15 cc.	3.18	0.00066

In mixtures containing 25 cc., or less, of the acid the *free* acid present is equivalent to that which dissociates from such protein compounds on solution in water.<sup>1</sup> Such concentrations of acid do not affect the trypsin in any marked degree, it appears. In fact, there may be even a little tryptic digestion in concentrations not greatly different from this, as will be shown in some of our work to follow, and as indicated by experiments of Michaelis and Davidsohn.<sup>2</sup> As stated, the acid values were found at the end of the three-hour digestion period, which is preferable to measurement at the outset. In making such mixtures some time elapses before an equilibrium is reached, as the combination between acid and protein is slow, unless they are ground together.<sup>3</sup> The initial concentrations might appear somewhat greater for this reason, and for the further reason that in a digestion like this the products formed in three hours would combine with a little more of the original acid.

In the later digestion in the slightly alkaline medium a hydrogen concentration of  $P_H = 8.0$  to 8.2, at the start, was found satisfactory. This was secured, in the present series of experiments, by the addition of something less than 4 cc. of normal carbonate for each 100 cc. of digesting liquid. No marked change in the alkalinity follows in a 20-hour digesting period, as illustrated by the short table below. Four mixtures were made up as in the regular acid digestions and carried through to the final di-

<sup>1</sup> Long, *THIS JOURNAL*, 37, 1333 (1915).

<sup>2</sup> *Biochem. Z.*, 36, 280 (1911).

<sup>3</sup> Long and Hull, *THIS JOURNAL*, 37, 1593 (1915).

gestion in alkaline medium. The hydrogen concentrations were found after the 20-hour period, as well as just before the beginning of incubation.

	Vol. of 0.1N HCl in prelim.	50 cc.	22.5 cc.	20 cc.	15 cc.
P <sub>H</sub> before incubation.....		8.0	8.0	8.15	8.15
P <sub>H</sub> after incubation.....		8.6	8.4	8.3	8.3

While the alkali concentrations formerly recommended for tryptic digestions, equivalent to about 0.5% of sodium carbonate, were too high for most mixtures, we have found that something less than half of this gives a good result. The limits need not be as narrow as claimed for the optimum activity by Michaelis and Davidsohn,<sup>1</sup> viz., P<sub>H</sub> = 7.68. Indeed, their own experiments seem to show that the rate of tryptic digestion is not much less at P<sub>H</sub> = 9. In the practical formaldehyde titration employed to measure the results there is some advantage in using the carbonate rather than phosphate mixtures. With these a longer preliminary treatment is necessary to bring the mixtures into condition for titration.

TABLE V.—PEPSIN-TRYPSIN DIGESTION WITH FIBRIN.

No.	Vol. of 0.1N HCl Cc.	Vol. of 0.2N NaOH. Cc.	A—A', etc.	General appearance.
A	50	8.4		All fibrin gone after peptic digestion. No digestion later
A'	50	8.4	0.0	As for A
B	45	7.5		As under A
B'	45	7.0	0.5	As under A
C	40	8.2		Peptic digestion only
C'	40	7.6	0.6	
D	37.5	7.7		Peptic digestion only
D'	37.5	7.4	0.3	
E	35	8.4		Peptic digestion only
E'	35	7.5	0.9	
F	32.5	8.0		Peptic digestion complete. A little change in second digestion
F'	32.5	7.3	0.7	Loss of fibrin in tryptic digestion
G	27.5	9.8		
G'	27.5	7.5	2.3	
H	25	11.0		Tryptic digestion
H'	25	7.0	4.0	
I	22.5	15.3		Tryptic digestion
I'	22.5	7.6	7.7	
J	20	15.6		Marked tryptic digest
J'	20	7.5	8.1	
K	15	17.4		Marked loss of fibrin in second digestion
K'	15	8.0	9.4	
L	00	27.5		Complete tryptic digestion
L'	00	8.6	18.9	
M	00	26.4		Complete tryptic digestion
M'	00	7.2	19.2	

<sup>1</sup> *Loc. cit.*

With these explanations of general relations which hold for all the mixtures to follow we present this table as showing the results of the digestions under the modified conditions.

L, L', M, and M' are straight tryptic digestions through 20 hrs. only, and with 3 grams of fibrin only. For the mixtures with boiled trypsin we have here rather large blanks, which come from the gradual solution or hydrolysis of fibrin through long contact with the weak alkaline liquid, and in which the protein dissolved is not thrown out by the final neutralization. But they come in part from the greater weight of soluble trypsin used here, as in these digestions the 500 mg. of trypsin was not divided into two portions, finally, as in the other cases. With this explanation it appears that the effect in K is almost as strong as in the L and M tests.

In comparing with Table IV it must be kept in mind that in that series the 100 cc. volumes with 500 mg. of trypsin were not divided at the end of the acid digestion, as here. In comparing the results in the above table among themselves it is evident that we have for the incubations with the higher acid concentrations peptic digestion only, plus the slight hydrolysis effect. As the acid concentration falls the higher titrations following the tryptic digestions become very apparent and the increase can be explained only through the activity of the residual trypsin. The H, I, J, K and L volumes differ from the H', I', J', K' and L' volumes only in this that the ferment was killed in the latter cases and not in the former. In the first set of flasks the trypsin, in part at least, must survive the acid incubation where this acid is diminished in activity by combining to a certain degree with the fibrin.

Attention must be called to the fact that the volumes of alkali used in the titrations of the contents of the flasks in which the trypsin had been killed before the final incubation are very constant throughout. This is interpreted as indicating the effect of the primary peptic digestion. But this view does not fully describe the situation. Even where there is no peptic digestion there is always some hydrolysis by reason of the long incubations, first in acid and then in alkaline medium, and the products remain in solution after the usual neutralization.

#### Series C. Casein Digestion.

In a manner similar to that shown for the fibrin digestions we have carried out a series of digestions with casein as the substrate, using in each case 1 g. of the pure dry substance in the preliminary incubations. The casein employed was made in the laboratory by the usual Hammarsten process and was light and easily soluble in the proper amount of weak alkali. A second gram was added for the tryptic digestions after the division of the original volume into two halves. Enough sodium carbonate was added to each flask to make a soluble salt of this casein and then the usual further amount to bring the reaction to the desired  $P_H$  value of

about 8.1. In the table below the boiled trypsin flasks are indicated by the prime letters, as before.

TABLE VI.—PEPSIN-TRYPSIN DIGESTION WITH CASEIN.

No.	Vol. of 0.1N HCl. Cc.	Vol. of 0.2N NaOH. Cc.	A—A', etc. Cc.	General appearance.
A	50	16.0		In all of the flasks the casein became pretty thoroughly digested in the acid incubation.
A'	50	11.6	4.4	
B	45	14.9		
B'	45	11.8	3.1	
C	40	15.5		After the tryptic digestion all the flasks appeared clear. Heavy neutralization ppts. came down in the blank flasks and in A, B and C; not much in D and E. Nothing in F, G, H.
C'	40	11.6	3.9	
D	35	22.4		
D'	35	11.7	10.7	
E	30	23.9		
E'	30	11.4	12.5	
F	25	26.8		
F'	25	12.0	14.8	
G	20	26.0		
G'	20	12.0	14.0	
H	15	25.8		
H'	15	11.9	13.9	
I	00	20.0		
I'	00	8.4	11.6	

The survival of the trypsin is clearly shown in the tests with the liquids containing the lower acid concentrations. The I experiments show the effects of tryptic digestion plus hydrolysis through the alkali in the long incubation. It is evident that this incubation can in time accomplish a part of the effect which is reached in the much shorter peptic digestion, as far as the amino acid titration is concerned. There appears to be some tryptic digestion in the flasks with even the highest acid concentrations, and this may be due to a greater initial combination of the protein with acid, leaving the latter less active in its trypsin destroying power. This will be illustrated in discussing the behavior of meat below. There is a second possibility here which must be referred to, and that is this that the trypsin may combine with the excess of protein in such a manner as to be protected more or less perfectly from the pepsin-acid action. This view will be taken up later.

#### Series D. Meat Digestion.

Three sets of tests have been carried out here, two with raw meat and one with cooked meat, and under the same general conditions as have been described for the fibrin and casein. The meat used in the raw condition was thoroughly washed to remove blood and easily soluble salts and then pressed out to eliminate the excess of water. In each case 4 g. were taken to make up the substrate and mixed with pepsin, trypsin and acid to make up a volume of 100 cc. as before. The digestions, neutraliza-

tions, division of the volume and addition of more meat for the tryptic digestions were carried out as before. These two sets of trials with raw meat were made six months apart and are reported separately to show about what degree of constancy may be expected under the conditions of the tests.

TABLE VIIa.—PEPSIN-TRYPSIN DIGESTION WITH RAW MEAT.

No.	Vol. of 0.1N HCl. Cc.	Vol. of 0.2N NaOH. Cc.	A—A', etc. Cc.	General appearance.
A	50	20.0		After the peptic digestion but little meat or other residue remained in any case, but there was always a precipitate on neutralization. After the tryptic digestion there was some meat left in all cases, in the unboiled as well as in the boiled flasks.
A'	50	11.2	8.8	
B	40	19.8		
B'	40	11.3	8.5	
C	35	20.6		
C'	35	11.1	9.5	
D	25	21.7		
D'	25	11.5	10.2	
E	23	23.8		
E'	23	11.3	12.5	
F	20	24.6		
F'	20	11.1	13.5	
G	20	25.0		
G'	20	11.0	14.0	

TABLE VIIb.—PEPSIN-TRYPSIN DIGESTION WITH RAW MEAT.

No.	Vol. of 0.1N HCl. Cc.	Vol. of 0.2N NaOH. Cc.	A—A', etc. Cc.	General appearance.
A	50	20.2		In the peptic digestion there was a practical disappearance of all the meat. The neutralization precipitate was small. In the following tryptic digestion there was meat left in all cases, from the second gram added.
A'	50	12.0	8.2	
B	45	21.0		
B'	45	13.4	7.6	
C	40	19.8		
C'	40	11.8	8.0	
D	35	20.5		
D'	35	13.0	7.5	
E	30	19.5		
E'	30	11.8	7.7	
F	25	21.7		
F'	25	12.0	9.7	
G	20	24.8		
G'	20	12.0	12.8	
H	15	28.8		
H'	15	11.5	17.3	
I	25	32.4		
I'	25	19.5	12.9	100 mg. of pepsin used.

At first sight it is apparent from these tables that a marked liberation of amino acid nitrogen occurs in the mixtures with the higher hydrochloric acid concentrations. To some extent this was noticed in the casein digestions; as distinguished from those with fibrin, but the dry casein

weights were a little larger than the dry fibrin weights which might account for a somewhat greater binding of acid. But such an explanation does not hold here where the action is pronounced. The four grams of moist, raw meat used in the initial incubations contained ordinarily less than a gram of actual protein. In grinding different lots of meat and washing as described, the Kjeldahl determinations have given amounts of nitrogen corresponding to a range of 0.9 g. to 1.0 g. of protein. A mean of 0.95 g. may be taken for the pulp employed here, which is a little greater than the fibrin weight. The acid-binding power of this meat is not greater than was found for the fibrin, as the following results of experiments conducted as were those with fibrin show. In each incubation 4 g. of meat with constant amounts of pepsin and trypsin and varying acid were employed.

Vol. of 0.1 N HCl in 100 cc.	P <sub>H</sub> .	C <sub>H</sub> .	Vol. of 0.1 N HCl in 100 cc.	P <sub>H</sub> .	C <sub>H</sub> .
50 cc.	1.74	0.0182	25 cc.	2.51	0.0031
35 cc.	2.06	0.0087	15 cc.	2.94	0.0011

In fact, the residual ion concentration, while small, appears to be greater than with the liquids secured from the fibrin experiments, from which it follows that the apparent tryptic activity in this case cannot be attributed to a lower hydrogen ion value, as was suggested above as a possibility.

It is well known that trypsin has a marked tendency to attach itself to certain protein groups and the meat proteins may have this binding and protecting power in a degree more marked than obtains with fibrin or casein. This brings us back to the hypothesis of Edie,<sup>1</sup> advanced to account for lowered pepsin activity in presence of trypsin, but the binding power of the protein may be just as important in holding and protecting the ferment as it is in holding the acid. In the one case we have a lowered hydrogen-ion concentration, while in the other the specific group of the ferment on which the acid may act destructively may be the one through which the ferment is linked to the protein. With high acidity this linkage would be broken with following destruction of the ferment. On the other hand, in the case of the low hydrogen-ion concentration, the stimulating value alone of these ions might come into play, with consequent solution of the protein linked up with the ferment.

The digestion tests with cooked meat were made in the same manner and with the same proportions. Since meat loses water in cooking the 4 g. taken for each mixture must represent a somewhat larger weight of real protein than is the case with the moist meat. The acid binding power would be correspondingly greater, which seems to show in some of the experiments.

<sup>1</sup> *Loc. cit.*



TABLE VIII.—PEPSIN-TRYPSIN DIGESTION WITH COOKED MEAT.

No.	Vol. of 0.1N HCl. Cc.	Vol. of 0.2N NaOH. Cc.	A—A', etc. Cc.	General appearance.
A	50	17.9		Most of the flakes of meat disappeared during the peptic digestion, but a fine sediment settled. A precipitate formed on neutralization which was larger than with the raw meat.
A'	50	10.0	7.9	
B	45	18.5		
B'	45	9.3	9.2	In the appearance of the flasks after the second digestion there was not much difference between the boiled and unboiled ferment portions.
C	40	17.6		
C'	40	9.3	8.3	
D	35	21.2		The trypsin ferment was killed in both I and I'.
D'	35	9.0	12.2	
E	30	19.8		
E'	30	8.7	11.1	
F	25	23.5		
F'	25	9.7	13.8	
G	20	25.1		
G'	20	10.0	15.1	
H	15	24.7		
H'	15	9.3	15.4	
I	15	9.5		
I'	15	9.5		

We have here the same general situation noticed in the digestions of the raw meat samples. In the trials with the weaker acid in the substrate the persistence of the trypsin is very apparent, while in the other cases the residual digestion is smaller but constant. In two experiments to determine the hydrogen concentration at the end of the peptic digestion of cooked meat under the conditions as obtaining above we found these results for liquids filtered from the flasks made up with 4 g. of cooked meat and 50 cc. and 25 cc. of the 0.1 N acid in 100 cc.

50 cc. flask.....	$P_H = 2.03$	$C_H = 0.00927$
25 cc. flask.....	$P_H = 2.61$	$C_H = 0.00245$

These degrees of acidity are so extremely small that we can well understand how the tryptic activity may persist to some extent. As pointed out in a previously quoted paper<sup>1</sup> peptic digestion begins to slow down at a concentration of hydrogen ions in the neighborhood of  $P_H = 2.60$ . The acid present is pretty well bound to the protein in these cases and not enough is free to seriously interfere with the trypsin.

In the discussions above the effects observed at the end of the initial incubation are spoken of as due to "peptic" digestion. This expression is used largely for convenience and includes the effects of simple incubation in producing hydrolysis under the conditions. The ordinary protein bodies when brought into solution in any manner show some acid groups by the formaldehyde titration, but in some cases the apparent effect may be due to the protein split products in the ferments themselves. It was formerly held that in the ordinary short pepsin digestion not many

<sup>1</sup> Long; THIS JOURNAL, 37, 1333 (1915).

peptide bonds are loosened in such a manner as to show anything in this titration. This view seems to have been held, for example, by Soerensen<sup>1</sup> himself, who introduced the general method. But enough work has been done since to demonstrate the value of the scheme in just such studies as the above. In a paper by J. Christiansen<sup>2</sup> some interesting information is given as to the extent of the preformed acid groups in some of the commercial ferments and the extent of the liberation of new groups by self digestion. The time element comes in here as an important factor.

But we are not concerned with the extent of the real peptic splitting in the initial incubation, or how much of the carboxyl measured here, by the titration after addition of formaldehyde, is due to a splitting just completed, as distinguished from the carboxyl of the ferments, etc. It is the *increase* of the carboxyl in the second incubation which interests, and under the conditions as brought out there seems to be no question as to the part taken by the trypsin here. All the results secured point in the same direction and to the conclusion that the pancreatic ferment persists through the acid incubation, provided this acid is sufficiently bound by protein to bring the hydrogen-ion concentration down to certain values.

This fact must have an important bearing on the answer to the practical question proposed at the beginning of the paper, which amounts to this: Will trypsin administered by the mouth persist in the stomach and retain sufficient activity to aid in proteolytic digestion in the duodenum? It is evidently true that trypsin when given in relatively large amount and in presence of protein possesses the degree of resisting power requisite for this. Not only does trypsin appear to resist the action of pepsin and acid under the conditions described above but it seems further likely that it is able to bring about some degree of digestion in acid solution which is more marked with some proteins than with others. This kind of activity toward fibrin seems to be less marked than with casein or meat, which may depend on some peculiar binding power or configuration in the fibrin complex as distinguished from the others.

It has been pointed out above that the work of Michaelis and Davidsohn<sup>3</sup> seems to indicate some slight degree of tryptic activity in low acid concentrations, while the same conclusion evidently follows from the studies of Mays<sup>3</sup> already quoted. That tryptic digestion, while greatly impeded in hydrochloric acid solutions, may go on very well in presence of lactic acid or weak acetic acid was shown in the investigations of Lindberger<sup>4</sup> who attempted to account for the protein digestion in the acid duodenal

<sup>1</sup> *Biochem. Z.*, 7, 45 (1907); 21, 289 (1909).

<sup>2</sup> *Ibid.*, 46, 50 (1912).

<sup>3</sup> *Loc. cit.*

<sup>4</sup> *Maly's Jahresh.*, 13, 280 (1883). From the Swedish. Reviewed at length by Hammarsten.

tract of the dog. At that period the relation of acidity to hydrogen-ion concentration was not known. Weak lactic acid furnished the proper medium for the purpose. The commonly accepted view that trypsin is readily destroyed by acids and that it can exert its peculiar behavior only in alkaline solutions follows, in part, from the assumed alkaline character of the pancreatic juice which is able to neutralize completely the acid chyme and leave a marked degree of alkalinity. Many recent observations have shown that the alkalinity of the pancreatic juice is often less than formerly considered "normal." The mixed duodenal fluid in dogs is frequently found to be not alkaline at all. It is also possible, as has indeed been frequently suggested, that for the initial solution and superficial splitting of the protein through trypsin a greater degree of alkalinity is called for than is favorable in the subsequent deep-seated loosening of peptide bonds. If the initial hydrolysis is accomplished through the action of pepsin and acid a nearly neutral medium might furnish the optimum condition for the later cleavage.

In recent papers by Long and Fenger<sup>1</sup> it has been shown that the press juice of the pancreas of hogs, sheep and cattle is distinctly acid and constantly so. More recent observations of Dr. Fenger of the Research Laboratories of Armour and Company and Mr. Nelson of this laboratory, as yet unpublished, have shown that in the juice of the duct of hogs, noted immediately after killing, the reaction is as often acid as alkaline. This undoubtedly bears some relation to the time of last feeding, but the result cannot be ascribed to the presence of traces of acid chyme which might have penetrated the duct from the duodenum. When expressed in terms of hydrogen-ion concentration the mixed duodenal fluid may, perhaps, be more often alkaline than acid, but the degree of alkalinity is so slight and so much lower than usually assumed that there appears to be no physiological necessity for the assumption that trypsin can act *only* in an alkaline medium, or that it is readily destroyed by weak acids of a concentration of physiological importance.

Coming now to a practical side of the discussion this observation is in order. While it is undoubtedly true that trypsin is able to withstand incubation with pepsin and acid in presence of protein sufficient to give a certain low resultant concentration of hydrogen ions, and while it is true that a certain degree of tryptic digestion may be possible in a medium in which the hydrogen-ion concentration is apparently greater than  $10^{-7}$  it does not follow that the practical value of tablets or powders containing a few milligrams of trypsin along with pepsin is worth considering. In the above experiments we have dealt with relatively large weights, and even greater amounts might have to be administered to have much effect in the conditions of the stomach. The most important factor in this

<sup>1</sup> THIS JOURNAL, 37, 2213 (1915); 38, 1115 (1916).

connection is not the absolute weight of hydrochloric acid or pepsin present but the relation of one to the other, and the resultant hydrogen-ion concentration.

### Summary.

It has been shown in previous papers from this laboratory, as well as by other investigators, that trypsin may be incubated with HCl of  $P_H = 1.5$  through half an hour or longer without appreciable loss of strength. In presence of pepsin the tryptic power is rapidly lost.

However, if sufficient protein is likewise present the acid, in combining with it, is unable to destroy in the same degree. When the acid concentration is reduced in this manner to  $P_H = 2.6$ , or below, tryptic activity persists, even through several hours at the temperature of the body. This is a practical condition which very commonly obtains in the human stomach. An active tryptic ferment would unquestionably pass with the chyme, in part at least, into the duodenum where the  $P_H$  value is quickly reduced to 6.5, or lower, and there be able to produce a normal proteolytic digestion of some degree.

From the above experiments it appears further likely that some actual protein splitting is accomplished by trypsin at a  $P_H$  concentration of 1.8 with certain types of proteins. The rapidity of this proteolysis must be slight, however, and the practical importance low.

Our thanks are due to Mr. H. V. Atkinson for assistance in part of this investigation.

CHICAGO, ILL.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY,  
No. 268.]

## EXPERIMENTS UPON THE AMYLASE OF *ASPERGILLUS* *ORYZAE*.

BY H. C. SHERMAN AND A. P. TANBERG.

Received June 19, 1916.

The amylase produced by the fungus *Aspergillus oryzae* has been known to science since about 1875 after having been used empirically in Japan for centuries. It forms the chief active constituent of taka-diastrase, introduced by Takamine in 1898,<sup>1</sup> which is prepared by growing the fungus on wheat bran, extracting with water and precipitating by the addition of alcohol in such quantity as to give a concentration of 70% alcohol by volume.

The present study was undertaken with the object of purifying the amylase as far as practicable and comparing its nature and properties

<sup>1</sup> *J. Soc. Chem. Ind.*, 17, 118.

with those of the pancreatic and malt amylases previously studied in this laboratory.<sup>1</sup>

The taka-diastase used as the starting point in our work consisted of three lots kindly furnished us by Parke, Davis & Company, and a smaller lot, of considerably higher diastatic power than the other three, for which we are indebted to Dr. Jokichi Takamine. These four lots are designated in the following pages as Samples I, II, III, and IV, and possessed diastatic powers ("new scale") of 18, 23, 18 and 118, respectively. The material was a fine, white or yellowish white powder. The first three samples were soluble to the extent of about eighty-five per cent., while Sample IV was almost completely soluble, in ten parts of cold water.

The starch used in all determinations of saccharogenic and amylolytic power was Merck's soluble potato starch prepared by the Lintner method.<sup>2</sup> The moisture which the air-dry starch contained was determined and allowed for. In determining activities of enzyme preparations allowance was also made for the slight reducing action of the starch upon Fehling solution. The very slight acidity of the starch was corrected by adding to each starch solution as prepared enough hundredth-normal alkali to make it exactly neutral to rosolic acid indicator.

In the use of triple-distilled water, special glassware, etc., and in the technique of determination of diastatic powers (both amylolytic and saccharogenic) the methods and precautions described in connection with previous work in this laboratory<sup>3</sup> were followed.

### Effects of Added Electrolyte.

In order to establish the conditions for determining the activity of this amylase a number of experiments upon the effects of added electrolytes were performed, since the statements on this point to be found in the literature appear contradictory and are in most cases only qualitative. In the present investigation the effects of the various electrolytes tested were studied by careful quantitative determinations of saccharogenic or amylolytic power in the absence of the electrolyte and in the presence of accurately measured additions in the same manner as in the experiments upon malt amylase previously reported.<sup>4</sup> For the sake of economy of space, however, the data of the individual measurements will not be reproduced here but only the general results obtained with each of the added electrolytes will be given.

**Upon the Saccharogenic Action, sodium chloride and potassium chloride** had very little, if any, effect. The activity seemed to be very slightly

<sup>1</sup> THIS JOURNAL, 32, 1073, 1087; 33, 1195; 34, 1104; 35, 1617, 1784, 1790; 37, 623, 643, 1305.

<sup>2</sup> Lintner, *J. prakt. Chem.*, [2] 34, 378.

<sup>3</sup> Sherman and Thomas, THIS JOURNAL, 37, 627, 628, 634.

<sup>4</sup> Sherman and Thomas, *ibid.*, 37, 628-641.

accelerated by these salts at a concentration of 0.0005 molar but the difference was scarcely greater than the probable error of experiment. At concentrations of 0.01 molar and above there appeared a very slight retarding effect. *Primary sodium* (or *potassium*) *phosphate* had no appreciable effect upon the saccharogenic activity of commercial taka-dias-tase, but when tested upon some of the purified amylase preparations described below, primary sodium phosphate in concentrations of 0.002 to 0.014 molar was found to have a slight accelerating action, the optimum being at 0.005 to 0.008 molar. *Hydrochloric* and *sulfuric acids* (tested upon commercial taka-dias-tase) appeared to have a scarcely perceptible accelerating action at very low concentrations, not above 0.0001 normal. At higher concentrations of these acids the action of the enzyme was retarded. *Phosphoric acid* exerted a similar scarcely perceptible activating effect at 0.0003 molar concentration and a retarding influence when added in larger quantity. *Secondary sodium phosphate* had a well marked inhibitory effect.

**Upon the Amyloclastic Action** the effects of added electrolytes were found to be qualitatively similar to the effects on saccharogenic activity, but quantitatively they were much more pronounced. On account of the relatively large experimental error, neither the optimum concentration of the electrolyte nor its quantitative influence upon the activity could be measured with any great exactness. *Sodium and potassium chlorides* at optimum concentrations of 0.02 to 0.08 molar augmented the amyloclastic action to about ten times that observed in the absence of added electrolyte. *Primary sodium and potassium phosphates* at concentrations of 0.02 to 0.026 molar also increased amyloclastic action about ten fold over that found without added electrolyte. *Hydrochloric and sulfuric acids* at concentrations of 0.0001 to 0.0002 normal increased amyloclastic action about eight fold. *Secondary sodium phosphate* had a decided inhibitory effect upon the amyloclastic action of the enzyme.

### Purification Experiments.

After the experiments described above had sufficiently established the conditions influencing the activity of this amylase, experiments were undertaken upon the purification of the enzyme, guided by quantitative measurements of the activity of the products obtained.

The material used in most of the experiments was commercial taka-dias-tase, but for a few of the latest experiments we used material of higher activity furnished by Dr. Takamine.

The method developed in this laboratory for the purification of pancreatic amylase<sup>1</sup> was first applied and yielded a product (Preparation 1) having a diastatic power of 150 ("new scale"). The method which had

<sup>1</sup> Sherman and Schlesinger, *THIS JOURNAL*, 34, 1105 (1912).

been found successful with malt amylase<sup>1</sup> was then tried. This product (Preparation 2) had a power of 90 ("new scale").

After these preliminary experiments, the purification was studied step by step, as follows:

**I. Fractional Precipitation with Alcohol.**—A study of the fractions obtained by the addition of increasing amounts of alcohol showed that the fraction of greatest activity was that which precipitated between 60% and 65% of alcohol (by volume). By a single such fractional precipitation it was possible to obtain a Preparation, 5a, with a diastatic power of 118. Dialysis with subsequent precipitation increased the power of this fraction to 128 (Preparation 8a).

**II. Fractional Precipitation with Alcohol and Sodium Chloride.**—In the course of the work on precipitation with alcohol it was found that often when the addition of alcohol alone was ineffective, a precipitate could be obtained on the addition of a little sodium chloride. In most of the later preparations sodium chloride was, therefore, used for this purpose, and was found, not only to increase the yield, but also to result in a more effective fractionation. Thus, in Preparation 14, the 60–65% alcohol fraction had a power of 179, and dialysis preceding the precipitation with alcohol and sodium chloride increased the power still further to 193.

It was also found in Preparation 12, that the sticky precipitates often obtained could be readily "hardened" by treatment with absolute alcohol and ether. This treatment not only facilitated the drying, but gave a material lighter in color and of slightly higher power. This procedure was followed, therefore, in all subsequent preparations.

In Preparations 17 and 19 the final precipitate was further fractioned into two parts, that precipitated at 60–62.5% and that at 62.5–65% of alcohol; but this additional fractionation did not result in any improvement of the final product.

Acetone was used instead of alcohol in Preparation 18, but no advantage was found in this modification of the method.

**III. Precipitation with Ammonium Sulfate.**—If the active material of taka-diastase is at all similar in chemical nature to the amylases of pancreatin and malt, the method of purification should include precipitation by some precipitant which would separate protein from carbohydrates. In Preparation 21 the procedure consisted in precipitation with ammonium sulfate, dialysis of a solution of the precipitate thus obtained and reprecipitation with alcohol. By this means there was obtained a preparation with a power close to 500, *i. e.*, about thirty times the diastatic power of the original material.

The fact that the highest power was obtained in the 60–65% alcohol

<sup>1</sup> Sherman and Schlesinger, *THIS JOURNAL*, 35, 1621 (1913).

fraction before precipitation with ammonium sulfate, and after such treatment in the 65-70% fraction, seems to indicate either that the other substances originally present exert a considerable influence upon the solubility of the enzyme in mixtures of alcohol and water, or that the nature of the active material is altered when it is precipitated and redissolved.

All of the preparations except those numbered 20, 22 and 23, were made from the three lots of commercial taka-diastase described above. In making these three (20, 22 and 23), Sample IV was used. This material gave by simple precipitation with alcohol and sodium chloride, a 60-65% alcohol fraction with a power of 392, while the procedure described above, involving precipitation with ammonium sulfate, yielded three precipitates with powers over 500.

### Data of Typical Experiments.

**Preparation 15.**—20 grams of Sample II dissolved in 200 cc. water; freed from insoluble residue by centrifuge; alcohol added to 60%, precipitate rejected, alcohol added to 65% and resulting precipitate dissolved in 65 cc. water; dialyzed in collodion sacs against 1000 cc. water for 37 hours at 5° to 7°, the dialyzate being changed at the end of 14 hours. The dialyzed solution was precipitated with 3 volumes of 95% alcohol, centrifuged and the precipitate washed with absolute alcohol and ether and dried in desiccator over sulfuric acid. Yield, 0.45 gram; Power 193 ("new scale").

**Preparation 20.**—10 grams Sample IV dissolved in 100 cc. water and purification continued as in Preparation 15 except that time of dialysis was 23 hours. Yield, 0.275 gram; Power 392 ("new scale").

**Preparation 21.**—10 g. Sample III, precipitated from solution in 100 cc. of water by 60 grams of ammonium sulfate. Precipitate dissolved in 80 cc. water, dialyzed against 800 cc. distilled water for 37 hours, with changes at end of 11 and 18 hours. Precipitated with alcohol and sodium chloride:

- (a) 0-60% (774 mg. sodium chloride)..... Power, 52.
- (b) 60-65% (325 mg. sodium chloride)..... Power, 191.
- (c) 65-70% (132 mg. sodium chloride), yield 0.1 g. Power, 498.

**Preparation 22.**—20 g. Sample IV, 200 cc. water, precipitated by 120 g. ammonium sulfate. Precipitate dissolved and dialyzed for 40 hours. Reprecipitated with alcohol as follows:

- (a) 0-60%..... Power, 209.
- (b) 60-65%, yield 0.5 gram..... Power, 502.
- (c) 65-70%, yield 0.2 gram..... Power, 545.

**Preparation 23.**—10 g. Sample IV, precipitated with ammonium sulfate, redissolved and reprecipitated with ammonium sulfate, dialyzed against distilled water, and precipitated as follows with alcohol and sodium chloride:

- (a) 0-60%..... Power, 108.
- (b) 60-65%..... Power, 236.
- (c) 65-70%, yield 0.1 gram..... Power, 535.

### Composition and Reactions.

The following table gives a brief summary of certain analytical data obtained on the three samples of commercial taka-diastase used, and on four laboratory preparations of increasing activity:



Designation.	Diastatic power. "New scale."	Moisture. %.	Ash (dry basis). %.	Nitrogen (calculated to dry, ash-free material). %.
Sample I.....	18	3.69	12.18	1.63
Sample II.....	23	3.33	14.95	2.69
Sample III.....	18	5.72	18.49	2.38
Preparation 10.....	81	7.10	5.39	3.81
Preparation 15.....	193	5.98	2.42	5.37
Preparation 20b.....	392	4.11	2.50	8.13
Preparation 22b.....	502	5.29	2.13	10.84

It will be noted that there is a very slight decrease in ash content as the power of the preparations increases from about 200 to over 500. The amount of ash in these preparations is comparable with that observed in malt and pancreatic amylase preparations obtained by somewhat similar methods of purification.

The increase in nitrogen content with increase in power shows that the substances which the purification process rejects contain less nitrogen than the enzyme-rich material which is retained, and suggests that the enzyme is composed either wholly or in part of nitrogenous material.

Especial interest attaches, therefore, to the behavior of the purified preparation when subjected to color reactions which are more or less characteristic of proteins as a group. The Hopkins-Cole test for tryptophan, the Millon reaction and the xanthoproteic reaction were applied to a typical purified preparation (No. 22) and all gave pronounced positive results.

This preparation also gave a blue-violet biuret test. When a solution of the material was boiled a coagulum appeared which gave a blue-violet biuret, while the filtrate from this coagulum gave a pink biuret test.

#### Relation between the Saccharogenic and Amyloclastic Powers.

In analogy with the comparison previously given of pancreatic and malt amylases,<sup>1</sup> the following data obtained on typical preparations made from taka-diastase are of interest:

Designation.	Power. "New scale."	Wohlgemuth figure.	"Amyloclastic power."	"Saccharogenic power."	Ratio.
Sample I.....	18	30,000	300	42	7 : 1
Preparation 15.....	194	266,600	2,660	438	6 : 1
Preparation 20b.....	392	715,000	7,150	880	8 : 1
Preparation 21c.....	498	910,000	9,100	1104	8 : 1
Preparation 22c.....	545	1,125,000	11,250	1200	9 : 1

"Amyloclastic power" shows the parts by weight of starch completely hydrolyzed to products giving no blue or violet color with iodine after digestion at 40° for thirty minutes.

"Saccharogenic power" shows the parts of maltose formed, at 40° in thirty minutes, by the enzyme acting on an excess of starch under

<sup>1</sup> Sherman and Schlesinger, *THIS JOURNAL*, 35; 1784 (1913).

the conditions described in the method for determining the saccharogenic power.

The figures show that the amylase of *Aspergillus oryzae* resembles pancreatic amylase qualitatively in that purification does not materially change the ratio of amylolytic to saccharogenic power. Quantitatively, the ratio is much larger than that observed in the case of pancreatic amylase, in the case of which the relation remains approximately constant at about 2 : 1.

### Stability.

No systematic study was made of the stability of solutions of taka-diastase or of amylase preparations obtained from it, but the following facts have been noted during the course of the investigation:

1. A solution of Sample I stood exposed for several days during the summer to a temperature of about 32° without any decrease in activity.
2. A solution of Preparation 12d, having a power of 104 at the time it was made up, had a power of 97 after standing in a refrigerator for seventeen days.

### Summary.

The Amylase of *Aspergillus oryzae* exerts its maximum activity, both amylolytic and saccharogenic, in a very slightly acid medium. Acid phosphate accelerates, while alkaline phosphate retards, the action.

Addition of neutral electrolytes, such as sodium and potassium chloride, to commercial taka-diastase, has no measurable effect upon the saccharogenic power, but does increase the amylolytic action.

The best preparations were obtained by extracting with water, precipitating with ammonium sulfate, dialyzing, and finally precipitating fractionally with alcohol. Such preparations have about thirty times the activity of the commercial material from which they are prepared, but are not so active as purified pancreatic amylase. They have higher amylolytic, but lower saccharogenic, power than the most active malt amylase preparations yet recorded.

The high ratio of amylolytic to saccharogenic power which is characteristic of commercial taka-diastase is shown in at least equal degree by the most highly purified preparations.

The purified material resembled the preparations of pancreatic and malt amylases in most of its chemical properties. It gave typical protein reactions when submitted to the Millon, xanthoproteic, tryptophan and biuret tests. Heated in water solution it underwent coagulation, and the coagulum and filtrate both showed the biuret reaction, the color being considerably pinker in the case of the filtrate than with either the coagulum or the original material. That its nitrogen content was lower than that of the best preparations of pancreatic and malt amylases may be due either to a difference in the chemical nature of the enzyme itself,

or to the presence of other substances which the methods of purification thus far developed do not wholly remove.

LABORATORY OF FOOD CHEMISTRY,  
NEW YORK, N. Y.

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### CORRECTION.

On page 1231, of the June number, in the first column of Table I, read "Conc. KCl" instead of "Conc. HCl."

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### NEW BOOK.

**Qualitative Analysis.** Vol. I of Analytical Chemistry, Based on the Eighth Edition in German by F. P. TREADWELL, PH.D. (Polytechnic Institute of Zürich). Translated and Revised by WILLIAM T. HALL, S.B. (Massachusetts Inst. of Technology). 4th Ed. xiii + 538 p. New York: John Wiley & Sons, Inc. Cloth, \$3.00.

The fourth edition of this well-known text on qualitative analysis merits favorable reception as a thorough and convenient laboratory guide. Treadwell-Hall always has been a favorite text, both for the student and the practical chemist, combining, as it does, compactness with sufficient detail. It is not too unwieldy for the student who wishes to go somewhat below the surface in this subject and still covers the ground sufficiently well to meet all the usual requirements of a reference text.

The scope and volume of this edition is, in general, the same as that of previous editions. The introductory or theoretical part covers 75 pages, 117 pages are devoted to the reactions of the cations, 138 to those of the anions, 32 to systematic analysis and 64 to the reactions of the rarer elements.

In revising the book for the 4th ed. Professor Hall has rewritten, and materially added to, the theoretical portion in particular. As stated in the preface, the text is not a literal translation of the German "Treadwell" although it is kept along the same general lines, and in sympathy with the views of Professor Treadwell. Other well-known texts, as Noyes, Stieglitz, Böttger and Ostwald have been drawn upon and indebtedness to these authors is acknowledged.

The theoretical portion is furnished with valuable tables (solubility products, oxidation potentials) and examples in connection with the discussion, which is clear and to the point. The present reviewer hails with pleasure the complete adoption, in this text, of the valence method for balancing oxidation and reduction equations. While there is room for discussion, in general, of the question whether oxidation can *actually* be represented by simple electronic transfer in every case, it is obvious in many cases, and probable in the majority, that this is the actual mechanism. At all events, whoever has had occasion to fight the bug-bear of oxidation and reduction reactions on the part of students, employing long-

winded and usually absolutely hypothetical component reactions, is likely to favor the much more elegant and direct valence-method which concerns itself with nothing else than the actual changes shown. With another detail of the text, namely, the adoption of specifically coined nouns for the various ions, the reviewer cannot find himself so much in sympathy. The German language, from which this usage is copied, lends itself admirably by form and custom to the coining of compound nouns such as "chlorion" and "iodion" but the English language does not lend itself in the same manner to this process and such terms as "diferrion," "triferrion" and "chlorosion" seem exotic and confusing instead of a simplification. In part this is also due to the fact that in English the ending "ion" is so frequently used in another connection. To exaggerate, a complex ion is thus logically a "complexion;" similar confusing terms are possible. This all, is, however, only a matter of personal preference, which will be decided by custom.

More space is devoted in this text to the reactions of the "acids" than to those of the "metals," which is not the usual practice, but is a step in the right direction. This portion of qualitative analysis usually receives short shrift in most texts in comparison with the importance of the material. The writer of this believes that the preponderance of attention given to the cations is the result of tradition and the difficulty of satisfactorily treating the anions, rather than a question of importance. The classification of the acids given in the text is the one most commonly used, that of Bunsen in 1878. The amount of space devoted here to the acids is perhaps an indication that in the future a satisfactory method for the systematic separation of the acids will be included in such works. One quite satisfactory scheme has already been devised by A. A. Noyes.

The mechanical details of the book are good and misprints are few (p. 35 chloride instead of chlorate, and 4 instead of 3), the type is clear and the illustrations well gotten up.

Even the most modest chemical library will find this volume a necessary addition.

H. C. P. WEBER.

# THE JOURNAL

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[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY OF WASHINGTON, D. C.]

## THE PETROGRAPHIC MICROSCOPE IN ANALYSIS.<sup>1</sup>

BY F. E. WRIGHT.

Received June 26, 1916

In science, as in business, no line of research or activity is entirely isolated and self contained, free to exist by itself and for itself, but it is related to, and dependent on, other branches of scientific or business endeavor. A discovery in one particular field of investigation is not limited to that field but may have profound bearing on many other fields. Similarly a new method or a new tool devised for a special purpose in one field may serve well other purposes in another field; thus the petrographic microscope which has been developed and used chiefly by geologists can be applied with success to many chemical problems. The purpose of the present paper is to indicate briefly some of these problems and to emphasize the function of the petrographic microscope in their solution.

The petrographic microscope was introduced half a century ago by geologists because chemical and mineralogical methods failed to furnish adequate information regarding the rocks. A chemical analysis gave the bulk chemical composition of a rock but did not indicate how the

<sup>1</sup> Presented before the Washington Section, Am. Chem. Soc., on Feb. 11, 1915; the Rochester Section on March 6, 1916; the New York Section on June 9, 1916; also in abstract before the Philosophical Society of Washington on Nov. 23, 1912.

several elements were distributed among the component minerals; chemical analyses of the soluble and the insoluble portions of a rock aided to some extent, but they were not adequate to meet the requirements of petrology. To know a rock thoroughly it was essential to know not only its chemical composition but also its mineral composition and its texture as expressed in the spacial grouping of the mineral components. This knowledge was obtainable only through the aid of the petrographic microscope.

In recent years the effort has been made, especially at this laboratory, to study from the standpoint of experimental geology the conditions of formation of minerals, rocks, and ores. This implies the artificial reproduction of these minerals and rocks and their identification under the petrographic microscope. In such work the time element is a most important factor. Rocks in nature form slowly and the crystals which develop have ample opportunity to grow to a fairly large size. In the laboratory, on the other hand, time is limited, the furnace charges are small, and the resulting crystallized aggregates are very fine grained. This has of necessity led to the development of petrographic microscope methods suitable for the accurate measurement of the optical constants of crystal grains measuring only 0.01 mm in diameter. With these methods it is now possible to measure readily and with sufficient accuracy the optical constants of a substance in particles so fine that in water they settle at the rate of only 30 cm. an hour, or in air at the rate of 25 cm. a minute. As the diameter of the particles in most materials and powders exceeds 0.01 mm. ( $\frac{1}{2500}$  inch), it is evident that this downward extension of the limits, to which petrographic microscope methods can be applied, has greatly increased the range of application and usefulness of the petrographic microscope. Up to the present time, however, such methods have been used in only a few chemical problems, but in each instance they have proved to be a most effective weapon of attack for the solution of difficulties which have heretofore been considered unsurmountable.

In this connection it may be well to emphasize the fundamental difference between the petrographic microscope and the ordinary chemical or biological microscope which has been used by chemists for many decades and which is essentially a magnifier and serves to render visible minute objects and details which would otherwise escape attention. Such objects are recognized by their shape, their size, and their color. In the case of bacteria the differences in their behavior toward certain stains aid in the diagnosis, while in other lines of investigation microchemical reactions serve the same purpose. The petrographic microscope, on the other hand, is not only a magnifier but also, and essentially, an optical instrument of precision for the measurement of the optical constants of substances either in thin plates or in powder form.

To illustrate this difference between the two types of microscopes by an example: Quartz ( $\text{SiO}_2$ ) is a colorless, transparent mineral crystallizing in hexagonal prisms and pyramids of such characteristic shape that this feature alone, when present, is sufficient to establish its identity. If quartz appeared invariably in such well developed crystals, the crystal habit would suffice for its determination and the ordinary microscope would answer the purpose well; and if all substances had different and equally characteristic crystal shapes the crystal-form alone would constitute an adequate basis for distinguishing substances. But this is of course not the case, for we can destroy external crystal form by crushing the crystal into bits. Each fragment of a quartz crystal is still quartz in spite of its irregular form. Under these conditions other properties inherent in quartz itself and not dependent on its outer form must serve for the determination. The chemist naturally turns to chemical composition, melting point, boiling point, solubility, etc., which are constants and are adequate for the identification of the substance if it be available in sufficient quantity and purity for the purpose. In the case of quartz and many other minerals the determination of these properties is, however, difficult and time-consuming, while in many fine-grained mixtures of different substances these properties are not ascertainable. Under these circumstances properties must be selected which can be determined on each crystal fragment, and these are preëminently the optical properties, which serve to distinguish with certainty between different substances, especially crystallized substances.

In a crystal the component atoms are arranged in orderly fashion as the result, during crystallization, of the action of the interatomic forces. These forces are different in different directions and are vectorial and polar in character; they find expression not only in crystal form but also in the vectorial behavior of a crystal toward any external system of forces, as light-wave forces, acting upon it. The physical properties of crystals vary in such definite manner with the direction that these properties and their variations serve as diagnostic features in the determination of crystallized substances. Thus on quartz fragments we can measure with the petrographic microscope the refractive indices for different wave lengths of light, the differences in refractive indices for any given wave length (birefringence), and the character and shape of the optic ellipsoid to which the several optical properties are referable. These data of measurement serve to render the determination of the fragments as quartz practically certain. It may be noted that there are only four optical properties of crystals which are ordinarily measured in determinative work and are expressed as numerical optical constants of a given substance. These are: the principal refractive indices, the principal birefringences, extinction angles, and the optic axial angle. Other optical

properties of diagnostic value, as color, absorption, pleochroism, elongation, optical character, dispersion of the optic axes, etc., are stated in more or less qualitative form.

Of these properties the refractive indices are the most important and fundamental and also the easiest to measure with the petrographic microscope. The refractive index is the ratio of the velocity of light in air to that in the given substance. The fact that different substances have different refractive indices enables us to use the refractive index as a basis for classification. For a given wave length of light a substance which crystallizes in the isometric system has only one refractive index; this index is the same for all directions in the substance and the optical surface of reference is a sphere. In other substances, as those of the hexagonal and tetragonal systems, the optical surface of reference is an ellipsoid of rotation; such crystals have two principal refractive indices. In still other crystals (orthorhombic, monoclinic, triclinic) there are three principal refractive indices and the surface of reference is a triaxial ellipsoid.

In the practical measurement of the refractive indices of the grains in a powder, the particles are immersed in liquids of known refringence and the refractive index of any given grain is compared with that of the enveloping liquid. These grains are more or less lenticular or prismatic in shape and when immersed in a drop of liquid on an object glass and placed on the microscope stage give rise to the phenomena of prismatic refraction. Under conditions of oblique or central illumination these phenomena are easily recognizable; and relative refringence determinations between liquid and mineral grains can be made with an accuracy of  $\pm 0.001$  under favorable conditions. This method requires a set of standard refractive liquids. A convenient set is one of mixtures so prepared that the refractive index of each successive liquid is 0.005 higher than that of the liquid preceding it.

The birefringence, another useful constant, is the difference between the principal refractive indices; it signifies a difference in the rate of transmission for plane polarized light waves vibrating along different directions in the crystal and this in turn gives rise to interference phenomena which are of value in determinative work. The strength of the birefringence of a crystal grain is estimated from its interference colors between crossed nicols. In colorless minerals like quartz the scale of interference colors is practically identical with Newton's color scale.

A birefracting mineral becomes alternately light and dark four times during a complete rotation of the microscope stage between crossed nicols. In many crystal sections these positions of darkness or extinction, as they are called, make definite angles with a crystallographic direction such as the trace of a cleavage plane. These are then called extinction angles and are a useful diagnostic feature.



A further important constant is the optic axial angle. Its measurement includes the determination of the angle between the two optic axes or binormals and also the determination of the character of the acute bisectrix, whether  $\alpha$  or  $\gamma$ , from which follows by definition the optical character, negative or positive, of the mineral. For most purposes a rough estimate of the size of the optic axial angle is sufficient.

These are the more important of the several optical phenomena which can be readily determined with the petrographic microscope on grains measuring at least 0.01 mm. in diameter. They may be used in the identification of any given substance, especially crystal grains or mixtures of different crystal fragments. In many cases the determination of only two or three of these constants is sufficient to establish the identity of a substance.

If in the field of chemistry the optical properties of all chemical compounds were known, as they are for the rock making minerals, it would be an easy matter for the microscopist to determine any given compound as such even in powder form and in the presence of other compounds. A chemical analysis in the case of mixtures may accomplish little because of the impossibility of separating the different compounds. Methods are available for estimating with the petrographic microscope the relative amounts of the different compounds which are present, and thus to make a fairly good quantitative analysis of a preparation.

In tests for homogeneity the petrographic microscope is especially valuable. By immersing the preparation in a liquid of the refractive index of the main crystal compound this compound practically disappears and any foreign material can then be detected at a glance. Solid solution can also be detected by these methods and in many instances a quantitative measure of the amount of solution in the crystal state can be obtained.

The fact that it is possible to measure accurately the optical properties of minute grains measuring only 0.01 mm. suggests at once many fields in chemistry for the application of petrographic microscope methods. Thus it may serve for the identification of chemical compounds in crystalline aggregates; it is also of value in testing the purity of a preparation, either a chemical precipitate, a drug, or other commercial product, as an abrasive, cleaning powder, tooth powder, baking powder, stones in glass, and a host of other products of similar type; in research work it is useful in the study of the phase relations in two, three, and polycomponent systems. For a given composition the primary phase is determined by chilling the preparation heated to a definite high temperature and examining the quenched product under the microscope. Measurements of the refractive indices of glasses of different composition in a given system enable the observer to trace step by step the change in the composi-

tion of the liquidus as crystallization proceeds and the final eutectic is approached. By thus combining thermal, chemical, and microscopical evidence it is possible to determine the equilibrium relations in poly-component systems with a high degree of accuracy, higher in fact than is possible in metal-component systems (alloys) even though these latter are better suited for thermal study. Without the aid of the petrographic microscope the attempt to ascertain the equilibrium relations in complex silicate systems is hopeless; with its aid each one of the three-component-systems studied in this laboratory has been brought to a successful finish; the degree of accuracy of the results can be ascertained in each case.

Experience has shown that these methods are applicable to the study and identification of all nonmetallic solid substances even though present in individual grains measuring only 0.01 mm. in diameter. It requires, of course, practice to apply these methods most expeditiously. In this respect the petrographic microscope is analogous to the lathe in the machine shop. The lathe in the hands of an instrument maker is a most successful instrument and remarkable results can be accomplished with it; and yet the principles on which it is based are not difficult to grasp. Similarly the petrographic microscope is equally useful in its line and its methods are simple and easy to apply for one who has had the necessary practice. One of the most difficult features of such work is the necessity of thinking in space. The optical properties of crystals vary with the direction and the observer must picture to himself the spatial relations involved if he would understand and take advantage of the phenomena he observes. This means, of course, a certain amount of training on the part of the chemist who would utilize this tool, but the saving of time and expense thereby gained more than compensates for the labor involved. It is fortunate that in most problems the determination of the refractive indices alone suffices for the diagnosis and that the method used for such determination is extremely simple and can be learned in a few hours' time and can be accomplished with the simplest type of petrographic microscope.

To cite a few examples of the application of petrographic microscope methods to chemical problems which have come within my own experience.

#### Identification of Chemical Compounds.

**The Osazones.**<sup>1</sup>—Of the osazones there are two in the pentose sugars; four in the hexose group; 8 in the heptose, etc. Within each group the identification by chemical means is difficult and in the pentose group it may be uncertain. In view of the many optical constants which can be ascertained, it should be possible easily to distinguish between the differ-

<sup>1</sup> Samples of the pentose and hexose osazones were kindly furnished to the writer by Dr. C. S. Hudson and Dr. La Forge of the U. S. Bureau of Chemistry.

TABLE I.

Name.	Melting point.	Habit.	Elongation.	Optical orientation.	$\alpha$ .	$\gamma$ .	Birefringence.	Remarks.
<i>Penulosazones</i>								
Xylosazone	160°	needles	+	$c = \gamma$ parallel extinction	1.745	1.860	strong	Characteristic green and yellow interference colors
Arabinosazone	160	long needles	—	$c = \alpha$ parallel extinction	1.765	1.870	strong	Abnormal interference colors
<i>Hexosazones</i>								
Allosazone	175	needles	+	$c = \gamma$	1.740	1.805	strong	Characteristic blue and orange interference colors
Galactosazone	208	needles in radial groups	$\pm$	$c : \gamma = 0^\circ$ to a large angle	1.825	1.850	medium	Strong dispersion of bisectrices. No position of extinction in white light. Interference color orange and green
Glucosazone	208	needles in radial groups	$\mp$	$c : \alpha = 0^\circ$ to a large angle	1.800	1.835	medium	Abnormal interference colors, green, blue, purple
Gullosazone	168	single needles	+	$c = \gamma$	1.670	1.820	very strong	Blue, green, and yellow interference colors

ent osazones by use of the petrographic microscope, even though only a few milligrams of material be available. The optical properties of the osazones, so far as determined, are listed in Table I; the determination of these suffices for the identification of any one of the pentose or hexose osazones.

A comparison of the properties of the two pentosazones shows that both are strongly birefracting, the arabinose showing abnormal interference colors and negative elongation while xylosazone crystals show characteristic green and yellow interference colors and positive elongation. The difference in the character of elongation of the needles is a diagnostic feature sufficiently characteristic to enable the observer to distinguish between the two pentosazones at a glance on a single needle weighing a small fraction of a milligram.

The hexosazones are likewise readily distinguished by their optical properties. In the case of galactosazone and glucosazone the differences in refractive indices and in character of elongation may be used as diagnostic features. The diagnosis in this case is, however, a little less easy than it is between other osazones. In Table I the refractive indices as listed are only approximately correct, but are adequate for diagnostic purposes. Characteristic for the entire group of osazones is the strong spectral absorption in the violet and blue-violet, and consequent lemon to orange yellow color.

**The Alkaloids.**<sup>1</sup>—The determination of certain alkaloids by chemical methods is not easy and may be exceedingly difficult in the case of mixtures. It is of interest, therefore, to note that their determination by petrographic microscope methods is, so far as can be judged from the writer's limited experience with such substances, a simple matter. It should be possible to prepare a table, similar to the tables used by petrologists for rock minerals, in which the optical properties of all known alkaloids are listed; by the use of such a table the microscopist can ascertain with certainty the different alkaloids present in a crystalline mixture or the degree of purity of a particular alkaloid in the case of a drug preparation. The optical properties, so far as determined, of the several alkaloids examined, are listed in Table II. Several of the alkaloids in the list were soluble in the refractive liquid employed and their refractive indices could not be determined accurately; but the values obtained are of the proper order of magnitude and suffice for diagnostic purposes. In case more exact data are desired a new set of refractive liquids chosen with special reference to the alkaloids is required.

Certain of the alkaloids in Table II are difficult to distinguish by chemical methods, especially if present in mixtures or in small amounts; their

<sup>1</sup> Samples of the alkaloids listed in Table II were kindly furnished to the writer by Dr. C. L. Alsberg, Chief of the U. S. Bureau of Chemistry.



optical properties are so different that a correct diagnosis under the petrographic microscope is relatively easy. In view of the importance of such work, especially in cases where only small quantities are available, it would seem that a thorough study of the whole group of alkaloids from this viewpoint is advisable.

**Homogeneity Tests.**—As noted above, the testing of the purity of materials can, in many instances, be accomplished best by the petrographic microscope. Thus these methods have been used in the examination and testing of sugars, salt, flours, drugs, photographic developing powders, chemical preparations and precipitates, organic and inorganic, and of many other products.

**Analysis of Commercial Products.**—There are on the market many preparations, such as baking and cleaning powders, abrasives, paints, fertilizers,<sup>1</sup> cements, etc., which are difficult to test adequately by chemical methods alone and in which a knowledge of the actual composition as revealed by the petrographic microscope may be of assistance. To cite an illustration: in Table III are listed the approximate compositions

TABLE III.

No.	Kind.	Abrasive.		Alkali.		Soap or fat.
		Maximum diameter in mm.	Per cent.	Kind.	Per cent.	
1	Powdered quartz.....	0.3	65	sodium carbonate	25	10
2	Powdered quartz.....	0.25	85	sodium carbonate	5-10	10
3	Crushed quartz.....	0.3	75	sodium carbonate as well- crystallized sal-soda	25	..
4	Powdered alkali-feldspar (microcline), some quartz....	0.15	85	.....	..	10
5	Powdered "pumice"-obsidian, slightly vesicular.....	0.25	80	sodium carbonate	5	10
6	Powdered "pumice"-obsidian similar to 5.....	0.25	40	sodium carbonate	5	10
	Powdered quartz.....	0.25	40			
7	Powdered "pumice"-obsidian similar to 5.....	0.25	40	sodium carbonate	5	10
	Powdered quartz.....	0.25	40			
8	Fine quartz silt, occasionally a larger grain of quartz....	0.25	5	sodium carbonate	20	..
				sodium bicarbonate	65	..

of eight common cleaning powders as ascertained by examination under the petrographic microscope. Many others, including soaps, etc., have been examined but the list is taken as representative of the several types. The total time taken for the examination of the eight samples was about two hours and the results listed are only first approximations sufficient

<sup>1</sup> See W. H. Fry, "Identification of Commercial Fertilizer Materials," U. S. Bureau of Soils, *Bull.* 97 (1914); also *Science*, N. S., 42, 89 (1915).

to establish the general character of the powders. In the table the optical properties of the different components are not listed, nor are certain characteristic features such as quality of crushing and sizing, purity of raw materials, etc.\* These are important and in case a given powder is to be used for a special purpose they determine in large measure its efficiency.

**Study of Equilibria Relations in Physical-Chemical Systems.**—In this laboratory petrographic microscope methods are applied primarily to the examination of the phase relations in two, three, and polycomponent systems, especially of silicates. The most detailed system yet solved is the system lime-alumina-silica.<sup>1</sup> In the course of this investigation microscopic examinations of over 5,000 heat treatments were made. The relations in this system are complicated and their elucidation required the combined attack of thermal and microscopic methods. Without the petrographic microscope the system could not have been solved; the solution was, however, of more than academic interest because of the fact that Portland cement clinker occupies a small area in one part of the diagram and the definite mineral composition of Portland cement clinker was unknown. Chemical methods alone were not competent to determine this mineral composition and it was not until after the introduction of petrographic microscope methods specially adapted to the study of fine grained preparations that we could hope for a satisfactory determination of its composition.

At present there is no text-book in which petrographic microscope methods are presented from the standpoint of this paper. Professor Chamot in his recent *Elementary Chemical Microscopy* devotes several chapters to the general description of petrographic microscope methods, but does not discuss them with reference to their applicability to fine grained materials. The writer is at present engaged in the preparation of a pamphlet in which these methods are to be presented in a form acceptable to chemists.

### Summary.

In this paper the function of the petrographic microscope as applied to certain classes of problems of a chemical nature is discussed in a general way and its usefulness in such work is emphasized. Attention is directed to the difference between the ordinary microscope which is only a magnifier and the petrographic microscope which in addition serves for the determination of the optical properties of minute crystal grains and plates measuring at least 0.01 mm. in diameter. The several optical properties thus used in diagnostic work are described briefly and the mode of their determination by means of the petrographic microscope is indicated.

<sup>1</sup> G. A. Rankin and F. E. Wright, "The Ternary System  $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ ," *Am. J. Sci.*, [4] 39, 1-79 (1915).

The single fact that it is now possible by means of simple petrographic microscope methods to ascertain the optical constants of minute crystal grains with sufficient accuracy for diagnostic purposes suggests a number of chemical problems in which the petrographic microscope may render useful service; a few such problems are noted above. In some instances, as in Portland cement clinker and in the set cement, the actual mineral composition and the physical-chemical phase relations can be ascertained only by means of petrographic microscope methods.<sup>1</sup>

Long experience with the petrographic microscope has convinced the writer that the field of its application is a large one and full of possibilities both from the viewpoint of pure research and of practical application in the technical world; in many instances information can be obtained by means of the petrographic microscope in a few moments which it would take several days to get by the usual methods; this means an appreciable amount of time and of money saved. To know at each step in a process or investigation just what is taking place is essential to effective work and such knowledge is obtainable in many problems only with the aid of the petrographic microscope.

WASHINGTON, D. C.

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[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY OF HARVARD UNIVERSITY.]

### DENSITY OF RADIO-LEAD FROM PURE NORWEGIAN CLEVEITE.

By T. W. RICHARDS AND C. WADSWORTH, 3D.

Received June 10, 1916.

Through the kindness of Professor Ellen Gleditsch of the University of Kristiania, we have been so fortunate as to receive a specimen of lead sulfide from carefully selected Norwegian cleveite. According to Dr. Gleditsch, "The Norwegian uraninites are very old and very unaltered. They are found in well developed crystals and occur in connection with the pegmatite dykes in southeastern Norway." The sample in question occurred in cubic crystals near Langesund.

As Hönigschmid has already pointed out,<sup>2</sup> the properties of radio-lead<sup>3</sup> obtained from pure minerals of this sort are far more interesting and significant than those of lead obtained from ordinary uranium ores, which doubtless contain some admixture of ordinary lead. Hönigschmid has shown that the lead from pure cleveite has an atomic weight as low as

<sup>1</sup> G. A. Rankin and F. E. Wright, *Am. J. Sci.*, [4] 39, 1-79 (1915); A. A. Klein and A. J. Phillips, "The Hydration of Portland Cement," U. S. Bureau of Standards, *Bull.* 43 (1915).

<sup>2</sup> Hönigschmid, *Sitz. Wien. Akad.*, 123, IIa, 20 (1914).

<sup>3</sup> The name radio-lead is used provisionally to designate lead which appears to be the result of radioactive transformation.



206.06, and our own experience with the sample referred to above essentially confirms this result, as will be shown in another communication. So far as we know, however, the density of lead of this kind has not yet been determined, and accordingly the present paper recounts such a determination, which forms an interesting sequel to the recently published results on the density of Australian radio-lead.<sup>1</sup>

The purification of the sulfide, which doubtless contained traces of sulfides of other metals, was carried out as follows: The specimen was dissolved in nitric acid and crystallized three times with centrifuging as nitrate,—a process which Baxter's experience has shown to be an excellent one for the purification of lead from other metals.<sup>2</sup> From this purified nitrate the chloride was precipitated by pure hydrochloric acid, and this salt was crystallized three times. The final crystals, after draining on the centrifuge, were stored in a vacuum desiccator over caustic soda. The chloride thus prepared was used for the determination of the atomic weight, the density being determined in the material saved from the filtrates from that determination. These filtrates contained excess of silver, therefore enough hydrochloric acid was added to bring the concentration of the dissolved chloride ion to 0.01 normal, because at this concentration silver chloride is most nearly insoluble.<sup>3</sup> When the precipitated silver chloride had settled and had been removed by filtration through a Gooch-Munroe crucible with platinum mat, the resulting solution was concentrated and crystallized once more as nitrate. The pure crystals were electrolyzed, and the pure radio-lead treated exactly as in the case of the other samples previously described.<sup>4</sup>

The amount of substance at hand being rather small, the work could not be done quite as accurately as before. The density determinations were made in the same pycnometer as before, by the second method described on page 223,—the volume of the pycnometer having been re-determined because its tip had been broken in the meantime. Four identical determinations gave 5.7200 as the weight of water in the pycnometer at 19.94°, weighed in air. Therefore, the volume of the pycnometer was 5.7361 cc.

TABLE.—DENSITY OF LEAD FROM CLEVEITE.

Obs. wt.	Wt. in vac. (W).	Obs. wt. water not displaced.	Corres. volume.	Volume of pyc.	Volume (V) of water displaced.	Density W/V.
4.4252	4.4250	5.3287	5.3437	5.7361	0.3924	11.277
4.4252	4.4250	5.3286	5.3436	5.7361	0.3925	11.274
4.4252	4.4250	5.3285	5.3435	5.7361	0.3926	11.271
4.4252	4.4250	5.3285	5.3435	5.7361	0.3926	11.271

Average, 11.273

<sup>1</sup> Richards and Wadsworth, *THIS JOURNAL*, 38, 221 (1916).

<sup>2</sup> Baxter and Grover, *Ibid.*, 37, 5 (1915).

<sup>3</sup> G. S. Forbes, *Ibid.*, 33, 1937 (1911).

<sup>4</sup> *Loc. cit.*, p. 224.

The density of this sample, presumably a nearly pure isotope, is thus 11.273, distinctly less than 11.289, the density of the Australian radio-lead, and still less than the density 11.337 found for ordinary lead. The decrease is almost exactly proportional to the decrease of the atomic weight in these samples, for the atomic weight of the Australian lead was about 206.35, and that of this sample 206.085. Thus the atomic volume of the isotope  $((206.08)/(11.273) = 18.281)$ , is almost identical with that of pure lead, as indicated by our previous experiments. 18.281 is essentially equal, within the limit of error of experiment, to the value 18.277, found for ordinary lead, and to the value 18.279, found for Australian radio-lead. It is interesting to note that Australian radio-lead would be essentially duplicated as to these properties by a mixture consisting of three parts of pure isotope to one of ordinary lead.

### Summary.

This brief paper describes the determination of the density of lead from Norwegian cleveite kindly furnished by Professor Gleditsch. This lead, presumably a pure isotope, was found to have a density (11.273) decidedly lower than the mixture previously studied. The corresponding atomic volume of the pure isotope is essentially equal to that of ordinary lead, as indicated by the earlier results on radio-lead from Australia.

CAMBRIDGE, MASS.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TEXAS.]

## AN ELECTRO-ANALYTICAL METHOD FOR THE DETERMINATION AND SEPARATION OF THE METALS OF THE COPPER-TIN GROUP.<sup>1</sup>

BY EUGENE P. SCHOCH AND DENTON J. BROWN.

Partly in collaboration with THOMAS E. PHIPPS.<sup>2</sup>

Received May 6, 1916.

Solutions containing chlorides have been considered unsuitable for the electro-analytical deposition of metals, probably on account of the oxidizing action of the liberated chlorine. Since the formation of chlorine can be prevented by the addition of reducing agents, and since such solutions present all the advantages of *simple acid electrolytes* while they are more serviceable than either the "sulfuric acid" or the "nitric acid" electrolytes advocated by Foerster<sup>3</sup> and by Sand,<sup>4</sup> respectively, it was decided to investigate their use with the more common metals, particularly with

<sup>1</sup> This work was carried out at the University of Texas under the direction of Professor Schoch and presented to the University of Chicago by Mr. Brown as part of the dissertation in partial fulfillment of the requirements for the Ph.D. degree.

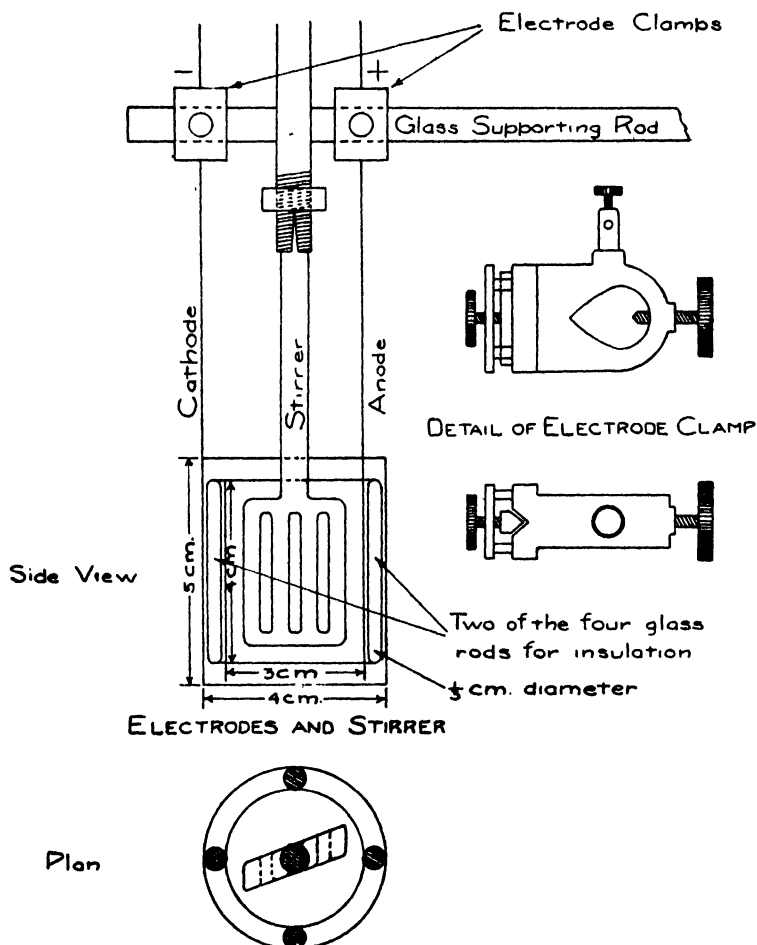
<sup>2</sup> Mr. Thomas E. Phipps worked out the methods given in Arts. 13, 14, 15, and 16.

<sup>3</sup> *Electrochemie Wässeriger Loesungen*, 23; *Z. angew. Chem.*, 19, 1842 (1906).

<sup>4</sup> *J. Chem. Soc.*, 91, 401 (1907).

bismuth, antimony, and tin. For antimony and tin the only method known heretofore which uses an acid electrolyte is that devised by Sand<sup>1</sup> and it requires the use of fairly concentrated sulfuric acid (sp. gr. 1.4), a temperature above 100°, and is altogether not as practicable or convenient a method as may be desired.

We have found that antimony, bismuth, copper, lead, tin and cadmium may be deposited quantitatively and in good form from "hydrochloric acid" electrolytes if suitable reducing agents are present in the solutions and oxides of nitrogen or nitric acid are absolutely absent; and that these electrolytes admit of the separation of all these metals from each other and from such other metals of the copper-tin group as would, if present, have to be considered.



<sup>1</sup> *J. Chem. Soc.*, 93, 1573 (1908).

### Apparatus and Manipulations.

**The Electrolytic Apparatus.**—In all of our work we used the Sand-Fischer apparatus and electrodes.<sup>1</sup>

The figure on p. 1661 presents the apparatus in detail. The introduction of a clamp of a special design made it possible to remove and replace quickly either of the two concentric electrodes without disturbing the other. This method of clamping eliminated the very undesirable glass tube formerly used for insulating the stem of the cathode, holds the electrodes more rigidly, and renders it possible to keep the electrodes suspended above the bottom of the beaker, thus permitting of more efficient stirring than is possible with the electrodes resting on the bottom. The electrodes were made of a fine platinum wire gauze—about 25 meshes to the cm. with a wire 0.1 mm. in diameter. The total surface of the cathode (or outer gauze cylinder) was estimated to be about 90 sq. cm. Hence the absolute values of the currents used are also very nearly the values of the current densities per 100 sq. cm. The most suitable beaker for the electrolyzing vessel was found to be a very tall or narrow beaker of 350 cc. capacity (height, 12½ cm.). With this beaker, the volume of electrolyte necessary to cover the electrodes is about 150 cc. The platinum anodes or cathodes were constantly reweighed during the progress of this work, and none of them decreased in weight during the operations mentioned in this paper.

The normal calomel electrode was employed as the auxiliary electrode in all of our determinations.

**Special Remarks on Manipulation.**—In the determination of metals that form alloys with platinum, *e. g.*, tin, lead and antimony, the platinum cathode was always covered with a deposit of copper before depositing the metal.<sup>2</sup>

Energetic stirring is essential to the success of these electro-analytical operations. Our stirrer made 800 revolutions per minute, but our apparatus was so rigid and the beaker so high that no loss through splashing was experienced. The sides of the beaker and the stirrer were always washed with a stream of water a short while before the end of a determination.

<sup>1</sup> For a general description of the apparatus and methods of determination by "graded potential" see texts on electroanalysis, *e. g.*, Smith, *Electroanalysis*, 274-84; Classen (translated by Hall), *Quantitative Analysis by Electrolysis*, Part I; Fisher, *Electroanalytische Schnellmethoden*. The apparatus we used was made by F. Koehler, Leipzig, Germany.

<sup>2</sup> If the deposit of copper is too thin, these metals pass through and unite with the platinum electrode. In such cases the general treatment for the removal of metal deposits will fail to remove all of the deposit. A remnant of antimony could be removed by heating the electrode to whiteness without loss of weight to the platinum electrode, but tin and lead cannot be removed by this method.

It was observed that all of our metal deposits, when covered by a film of the electrolyte, oxidize quickly on exposure to the air. Hence a special effort was made to remove the electrolyte quickly and effectively from the cathode. If the electrolyte was to be employed for the determination of a second metal, the deposit was washed with a stream of water while the beaker was lowered away from the electrodes. If no other quantitative determination was to be made, a beaker of distilled water was quickly substituted for the electrolyte. The deposit was then washed successively in alcohol and in ether and finally dried by holding it high above a Bunsen burner flame.

All metal deposits, except those of antimony and tin, can be removed by means of nitric acid, but antimony and tin form oxides which adhere so tenaciously to the electrodes that they require the use of a brush to remove them. Hence these metals were removed electrolytically by connecting the electrode with the deposit as an anode in dilute hydrochloric acid. Antimony can also be removed by means of a mixture of nitric and tartaric acids. Lead peroxide is removed by means of a mixture of nitric and oxalic acids.

All metal deposits can be removed by immersing them in a mixture of concentrated hydrochloric acid and water (1 : 1), adding nitric acid—a few drops at a time—and proceeding as directed below under “Preparation of Electrolyte.” This method of redissolving metal deposits was employed particularly for dissolving mixtures which required further separation.

**Préparation of Electrolyte.**—As the determination of very small amounts of any metal to be deposited is in reality the same as the determination of the last portions of larger amounts, no special determinations were made with minute quantities of metals, and the samples were all chosen so as to contain, of the metals to be deposited, the largest amounts suitable for these determinations. Whenever other metals than those to be deposited were added, they were also added in the largest proportion in which they are ever likely to be present in a practical analysis, because the probability that the deposited metal may be contaminated by other metals becomes greater as the amounts of such other metals in the electrolyte becomes greater.

The purity of the substances used for samples was always ascertained by the usual qualitative tests, in addition to the careful observation of the quantitative results attained. When pure metals were not obtainable for samples, they were either prepared electrolytically—as in the case of bismuth—or some pure definite compound of the metal was used, *e. g.*, antimony oxide, recrystallized arsenious oxide, etc.

We weighed out as much of the sample as would give a deposit of at least a tenth of a gram of any constituent, but would not give a total for

any single deposit greater than two-thirds of a gram. To this we added 8–12 cc. of concentrated hydrochloric acid (sp. gr. 1.20) and an equal amount of water. Samples consisting of tin or of more reactive metals were placed in contact with platinum, under which conditions they dissolve rapidly, but if lead or metals more noble than lead were present, we added a few drops of nitric acid, not sufficient to react with the whole sample, and warmed the mixture slightly—not above  $75^{\circ}$ —in order to prevent the loss of volatile chlorides. Since it is very essential that the mixture is not overheated—even momentarily—we placed the beaker in a water bath kept at about  $70^{\circ}$  or we placed it inside of a larger beaker containing some water warmed to  $70^{\circ}$ . When the reaction ceased, we added more nitric acid, a drop at a time, and allowed each portion to react completely before adding the next one; this we continued until the whole sample had been attacked with the least possible amount of nitric acid. An excess of nitric acid is to be avoided because it will prevent the complete deposition of the metals, and can not be removed completely even by the addition of such active reducing agents as hydrazine or hydroxylamine hydrochloride. Its removal by evaporation is generally not practicable because the chlorides of several metals of this group are volatile, *e. g.*, the chlorides of arsenic, antimony and tin.

Next we added 2 g. of hydroxylamine hydrochloride (to remove the oxides of nitrogen and the free chlorine), and heated the mixture as before, not to exceed  $70^{\circ}$ . The mixture was then diluted to 150–200 cc. to suit the size of the electrolytic vessel, and electrolyzed according to the methods presented below. Some of the experimental work was done with solutions prepared in ways different from the above. Special mention will be made of this fact wherever that was the case.

### **The Systematic Separation of the Metals of the Copper-Tin Group.**

The ultimate object of this investigation is the devising of a system for the electro-analytical separation and determination of all the common metals. The work in this paper together with some well-known analytical facts has practically enabled us to attain this object; and since the data to be presented in this paper owe a large part of their value to the fact that they fit into such a scheme, we have decided to present an outline of such a scheme here. The outline will show the relation of the different experimental results to each other and to the whole.

If arsenic is present, the sample should be dissolved as outlined above, somewhat more hydroxylamine hydrochloride (a total of 3 g.) should be added, the concentrated mixture should be transferred to a 200 cc. distilling flask (with the aid of concentrated hydrochloric acid to “wash” the remnants into the flask, or better, the whole previous treatment is made in this flask), and the arsenious chloride is distilled while a current of hydrogen chloride gas is passed through the distilling flask (Fischer's

method).<sup>1</sup> The distillation should be continued until the residue in the distilling flask has a volume of 10 to 20 cc. It should be mentioned here that if antimony is present, a small amount of antimonous chloride may distil over, and will be determined together with arsenic if the latter is determined by titration with iodine; but this trace of antimony can be conveniently separated from the arsenic by Bunsen's method<sup>2</sup> and determined, or added to the residue left after distillation.

If the residue left in the distilling flask is less than the original volume (20 to 25 cc.), it should be brought up to this volume by the addition of a mixture of equal parts of water and concentrated hydrochloric acid.

The residue from the arsenic distillation is rinsed into an electrolysis beaker, and is then diluted as necessary for electrolysis. Of course, if arsenic is not present, the original concentrated solution is thus diluted. If a precipitate of mercurous chloride, of silver chloride, of gold or of platinum is present, the concentrated mixture should be diluted only partially, filtered, the precipitate washed, and the filtrate plus the washings diluted further until the solution has the volume necessary for electrolysis (150-200 cc.).

If the precipitate on the filter paper contains silver chloride, it should be treated with ammonia. Silver may be deposited quantitatively out of this solution in ammonia by a method elaborated recently in this laboratory, and presented under a separate heading at the end of this paper.

Any mercurous chloride, gold or platinum remaining on the filter may be separated and determined by well-known methods.

From the solution obtained as above described, the first metals to be deposited with the least electromotive force, will be bismuth, copper or antimony. These three metals are deposited under practically the same conditions; hence, if more than one of them is present in the electrolyte, they will be deposited together according to the directions given in Sections 13, 12, 11, 6, 5, 4, 3 or 2. The first section here mentioned presents the general method in its final form, usable with all metals present, while the other sections present the general method in the earlier form, or methods usable when only certain metals are present. These metals may be separated by methods given in Sections 16, 15, 14 or 10.

After the removal of the above metals, the next metals to be deposited from the electrolyte are tin and lead. These metals are deposited under practically the same conditions; hence will be deposited together if both

<sup>1</sup> This procedure was tested quantitatively in this laboratory by Mr. R. M. King. The apparatus and procedure employed is essentially identical with that recently published in *J. Ind. Eng. Chem.*, 8, 329 (1916), except that we passed a current of hydrochloric acid gas through the apparatus, while the directions in this reference call for the addition of concentrated hydrochloric acid. The latter probably makes the operation more convenient.

<sup>2</sup> See Classen, *Quantitative Analysis* (translated by Harriman) ed. 1902, p. 89.

are present in the electrolyte. For details see Sections 9, 7 or 1. This alloy is readily separated by the method in Section 8.

Cadmium is the last metal in this list to be deposited from the electrolyte after the removal of the metals above. No metals "more zincic" than cadmium are considered in this outline. The term "more zincic" is employed, in preference to "more negative," to signify that the element is more active as a metal, or has a greater tendency to form positive ions—"more like zinc."

Since the relations of the facts presented in this paper are shown by the outline, it is unnecessary to indicate them again; hence we will present our results in the order in which they were obtained rather than in the order which would conform to the outline. A list of the different determinations—or section headings—is given here for convenient reference.

1. The Determination of Tin:
  - (a) General Method.
  - (b) A Modification of Classen's Oxalate Method.
2. The Determination of Copper.
3. The Separation of Copper from Tin.
4. The Determination of Bismuth.
5. The Determination of Antimony.
6. The Separation of Antimony (or Bismuth) from Tin.
7. The Determination of Lead.
8. The Simultaneous Deposition of Lead and Tin and their Separation.
9. The Separation of Tin from Cadmium.
10. The Separation of Copper from Antimony.
11. The Simultaneous Deposition of Copper and Antimony out of an Electrolyte Containing Copper, Antimony and Lead, and the Separation of Copper from Antimony by means of Nitric-Tartaric Acid Electrolytes.
12. The Simultaneous Deposition of Copper, Bismuth and Antimony out of an Electrolyte Containing these Metals and Tin: General Method.
13. The Simultaneous Deposition of Copper, Bismuth and Antimony out of an Electrolyte Containing These Metals and Also Tin and Lead.
14. The Separation of Bismuth from Antimony.
15. The Simultaneous Deposition of Copper and Bismuth from a Solution Containing these Metals and Antimony.
16. The Separation of Bismuth from Copper by Precipitation of the Former as Bismuth Phosphate.

1. (a) **The Determination of Tin: General Method.**—Copper plated cathodes were used for all depositions of tin.

Preliminary experiments showed that in the absence of reducing agents the greater part of the tin present in a solution of stannous chloride acidified with hydrochloric acid can be deposited rapidly in excellent form, but that the remnant could not be deposited even when the current was increased or continued for a long time. In fact, the tin finally dissolved more rapidly than it was deposited, until all the tin was redissolved. This was undoubtedly due to the high concentration of chlorine in the solution after long electrolysis, because when a suitable reducing agent



is present in the electrolyte, the tin is deposited quantitatively. These trials indicate that chlorine is the main cause why many metals cannot be deposited completely from chloride electrolytes.

In the following determinations "Analyzed" pure tin was dissolved cold, in approximately 10 cc. of hydrochloric acid, sp. gr. 1.20, in contact with metallic platinum. After the addition of the reducing agent, the resulting solution was diluted to approximately 200 cc. and electrolyzed.

The maximum current density, with which a good deposit of tin may be obtained out of the "hydrochloric acid" electrolyte, *decreases* as the concentration of the tin salt *increases*. With amounts of tin as high as 0.7 g. in 200 cc., a current of 1.5 amperes gave, with the electrodes employed, a good deposit at temperatures ranging from 30 to 70°. With higher current densities, the relatively concentrated solutions gave granular deposits, and even "trees," but less concentrated solutions gave good deposits even with somewhat higher current densities. Since 0.7 g. would be as large an amount of tin as would be used ordinarily for analysis, and as 1.5 amperes may be safely used with this concentration of 0.7 g. in 200 cc., this amount of current was used at the start in all the determinations of tin.

The "end point" was determined by ascertaining whether or not an increase in the weight of the deposit was obtained upon replacing the electrode in the electrolyte, and electrolyzing further. The result was also confirmed by qualitative tests.

TABLE I.

Reducing agent.		Time. Minutes.	Tin.		
Substance.	Grams.		Present.	Found.	Error. %.
NH <sub>2</sub> OH.HCl.....	4	95	0.4370	0.4380	+0.23
		90	0.2460	0.2466	+0.24
		90	0.6972	0.6970	+0.03
		120	0.3046	0.3052	+0.20
		120	0.3000	0.3000	0.00
(COOH) <sub>2</sub> .2H <sub>2</sub> O.....	10	75	0.3580	0.3572	—0.24
		75	0.3830	0.3822	—0.22
		85	0.2070	0.2064	—0.29

A comparison of the results obtained with these and other reducing agents is of special interest. With hydroxylamine hydrochloride, tin is deposited completely and in a comparatively short period of time. With oxalic acid, a trace of tin always remains in the electrolyte, that is, the tin is deposited almost, but not quite, completely. With formaldehyde the deposition is decidedly incomplete, though more extensive than would be the case if no reducing agent were employed. The fact that with formaldehyde the deposition is incomplete is rather surprising because, in some respects, formaldehyde is a stronger reducing agent than hydroxylamine; but this anomaly may be due to the fact that formaldehyde acts as an

oxidizing agent towards energetic reducing agents; hence perhaps toward stannous chloride.

1. (b) **A Modification of Classen's Ammonium Oxalate Methods for the Determination of Tin.**—It is well known that tin may be completely deposited out of a solution to which both ammonium oxalate and oxalic acid have been added. However, the oxalate methods heretofore employed have some undesirable features: the procedure recommended by Classen<sup>1</sup> gives an excellent deposit, but requires a long period of time (nine hours); while Exner's<sup>2</sup> rapid method requires the use of a "hot saturated" solution of ammonium oxalate, which is somewhat troublesome to handle, and the deposit is loosely adherent and powdery. Hence an improvement of the "oxalate method" is desirable. Since we found that the maximum current density with which a good deposit may be obtained from Classen's oxalate electrolyte increases as the concentration of the tin decreases, we concluded to combine this fact with the fact stated at the beginning of the determination of tin, namely, that even in the absence of a reducing agent tin may be deposited almost completely from a chloride electrolyte. The new "oxalate method" thus devised is carried out as follows: The greater part of the tin is deposited rapidly out of the simple "hydrochloric acid electrolyte to which no reducing agent has been added;" then the ammonium oxalate and oxalic acid are added and the remnant of the tin is deposited fairly rapidly. A current of 1.5 amperes may be used during the whole determination. "Time I" in the table below shows the number of minutes during which the original "hydrochloric acid" solution was electrolyzed and "Time II" the number of minutes during which the solution was electrolyzed after the ammonium oxalate and oxalic acid have been added. The modification places this "oxalate method" in the list of "rapid methods."

TABLE II.

Substance, grams.		Time, minutes.		Tin.			
(NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub> .	H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> ·2H <sub>2</sub> O.	I.	II.	Total.	Present.	Found.	Error. %.
4	10	45	45	90	0.3112	0.3114	+0.06
7	10	45	45	90	0.3088	0.3092	+0.13
7	18	60	45	105	0.3157	0.3156	—0.03
7	18	60	45	105	0.3542	0.3537	—0.13
7	18	75	45	120	0.4852	0.4849	—0.06
10	18	80	55	135	0.6838	0.6834	—0.06
7	16	45	45	90	0.3550	0.3550	0.00
7	17	45	45	90	0.2674	0.2675	+0.04
4	10	45	30	75	0.2608	0.2606	—0.08

2. **The Determination of Copper.**—It is impossible to deposit copper in good condition from a simple solution of cupric chloride acidified with

<sup>1</sup> See Classen-Hall, "Quantitative Analysis by Electrolysis," 1913, p. 136.

<sup>2</sup> See Smith, "Electroanalysis," 1907, p. 168.

hydrochloric acid, but in the presence of suitable reducing agents copper can be deposited quantitatively and in excellent form, provided the concentration of the copper does not exceed 0.4 g. per 100 cc.—which is from 0.6 to 0.8 g. for the usual volume employed—with greater concentrations of copper, no electrolytic deposit is obtained.

The "most zincic" cathode potential with which copper could be obtained in good form is approximately  $-0.60$  volt against the "normal calomel electrode." This is practically the potential at which hydrogen is evolved from this electrolyte on copper; hence the appearance of hydrogen may be used to limit the applied voltage. The determinations below marked "hydrogen limit" have been made in this way, that is, by keeping the current or voltage just low enough to avoid the evolution of hydrogen. The least "zincic" cathode potential with which copper may be practically completely deposited is  $-0.40$  volts against the calomel electrode, but frequently 0.1 to 0.3% of copper cannot be deposited at this potential and in general complete deposition is secured only with a cathode potential of  $-0.50$  volt. This potential just barely admits of the separation of copper from tin or lead. Naturally, when the cathode potential is limited at any value between  $-0.50$  and  $-0.40$  volt, the deposit of copper is certain to be free from tin or lead, but a few tenths per cent. of copper may not be deposited.

Metals more "zincic" than tin or lead are kept out of the copper deposit by not allowing the cathode potential to become more zincic than  $-0.60$  volt or by keeping the potential below that with which hydrogen begins to be evolved.

The salts of none of these "more zincic" metals, except those of iron, exert any specific effect; but iron salts prevent the deposition of copper, unless hydroxylamine hydrochloride is employed as the reducing agent.

In connection with the selection of suitable reducing agents for copper, we found that a weak reducing agent such as tartaric acid could be used for its separation from cadmium, nickel, cobalt, chromium and manganese, but that more time is required when this reducing agent is employed than when one of the more active reducing agents, such as formaldehyde or hydroxylamine hydrochloride, is employed. Hydroxylamine hydrochloride is really the only reducing agent that gave good results under all conditions; hence we have used it rather generally.

Special attention is here called to the fact that the behavior of the cathode potential during the deposition of a metal furnishes the operator a reliable automatic indication of the "end point." As the amount of the metal ion in the solution decreases and finally becomes zero, it is necessary to reduce the applied voltage so that the current finally reaches a low "residual" value, or becomes practically zero. In our work the "end points" were all ascertained in this way, which accounts for the differences in the re-

TABLE III.

Other metals present.	Reducing agent. Subst.	Volts.		Against HgCl electrode.	Amp.		Time.	Copper.		Error. %.
		Max.	Min.		Max.	Min.		Present.	Found.	
.....	Formalin 10 cc.	2.0	1.6	-0.40	3.0	0.05	45	0.2700	0.2698	-0.07
.....		2.0	1.6	-0.40	3.0	0.05	50	0.3722	0.3720	-0.05
.....		2.0	1.6	-0.40	4.0	0.05	30	0.3084	0.3080	-0.13
.....		2.0	1.6	-0.40	4.0	0.05	30	0.3962	0.3960	-0.05
.....		2.0	1.5	-0.40	7.0	0.0	180	0.5194	0.5196	+0.04
.....		2.3	1.3	-0.40	8.0	0.0	70	0.3292	0.3298	+0.18
.....		2.1	1.5	-0.40	7.0	0.0	150	0.3785	0.3780	-0.14
.....		2.1	1.5	-0.40	6.0	0.0	70	0.3642	0.3650	+0.22
.....		2.1	1.5	-0.40	7.0	0.1	130	0.4624	0.4616	-0.16
.....		2.0	1.5	-0.40	6.0	0.1	160	0.3000	0.2995	-0.17
Ammonia.....		2.2	1.5	-0.40	7.0	0.0	75	0.4320	0.4316	-0.09
Ammonia.....		1.9	1.5	-0.40	4.0	0.0	140	0.3411	0.3412	+0.03
Potassium.....	Tartaric acid 10 g.	1.8	1.5	-0.40	3.0	0.0	180	0.5520	0.5510	-0.19
Potassium.....		2.3	1.5	-0.40	6.0	0.0	60	0.5650	0.5640	-0.18
Cadmium.....		1.0	1.5	-0.40	4.0	0.0	85	0.2535	0.2528	-0.28
Nickel.....		2.0	1.5	-0.40	4.0	0.0	60	0.5120	0.5118	-0.04
Cobalt.....		2.0	1.5	-0.40	4.0	0.1	180	0.5072	0.5070	-0.04
Chromium.....		2.1	1.5	-0.40	6.0	0.0	205	0.5618	0.5612	-0.10
Chromium.....		2.0	1.5	-0.40	4.0	0.0	190	0.4222	0.4222	±0.00
Manganese.....		2.1	1.2	-0.40	6.5	0.0	30	0.7342	0.7328	-0.18
None.....		2.1	1.4	-0.40	7.5	0.0	30	0.6136	0.6139	+0.05
None.....	NH <sub>4</sub> OH.HCl 2 g.	2.0	1.2	-0.40	4.0	0.0	20	0.2922	0.2918	-0.13
None.....		2.0	1.2	-0.40	4.0	0.0	15	0.3552	0.3548	-0.11
None.....		2.0	1.2	-0.40	5.0	0.0	15	0.4016	0.4015	-0.03
None.....		1.6	1.5	-0.40	3.0	0.0	30	0.3485	0.3486	+0.03
Iron.....		1.6	1.3	-0.40	4.0	0.0	60	0.4024	0.4022	-0.04
None.....		2.5	1.0	-0.60	10.0	0.0	10	0.4232	0.4230	-0.04
None.....		2.4	1.65	-0.60	8.0	0.0	25	0.4094	0.4100	+0.15
None.....		2.2	1.65	-0.60	7.0	0.0	35	0.4006	0.4000	-0.15
None.....		2.35	1.65	-0.60	8.0	0.0	20	0.3426	0.3426	±0.00
None.....		2.5	2.0	-0.60	10.0	0.1	45	0.6320	0.6318	-0.03
None.....	Formalin 10 cc.	1.8	1.4	Hydr. Limit	2.0	0.05	45	0.4378	0.4374	-0.04
None.....		1.8	1.6	"	2.0	0.05	50	0.2598	0.2598	±0.00
None.....		1.6	1.2	"	2.0	0.05	60	0.2880	0.2882	+0.06
None.....		1.5	1.5	"	..	..	25	0.4388	0.4392	+0.09
None.....	NH <sub>4</sub> OH.HCl 2 g.	1.5	1.5	"	..	..	45	0.4040	0.4038	-0.04
None.....		1.5	1.5	"	..	..	50	0.6463	0.6454	-0.15

quired lengths of time given in the table of results below. We note that the minimum lengths of time for the determination of copper were required when hydroxylamine hydrochloride was employed, which is another reason why we believe that this is the most suitable reducing agent for these determinations.

Sometimes copper will not begin to be deposited immediately when the current is turned on. This is usually due to the fact that too much nitric acid has been used in dissolving the sample. Occasionally the disturbing factors are removed by the passage of the electric current, but generally the trouble is irremediable. This is true not only for the deposition of copper but for the determination of other metals.

The solution usually becomes clear long before the copper is completely deposited; this is due to the conversion of the cupric salt to cuprous salt, and should not mislead the experimenter into believing that the copper is nearly all deposited. A qualitative test for copper should not be attempted for a long time after the blue color has disappeared, because the liquid removed for testing cannot be returned to the electrolyte.

Pure electrolytic copper was used for the determinations below. The electrolyte was prepared by the general method described above. Besides hydroxylamine hydrochloride, various other reducing agents were used with copper, as the experiments show.

**3. The Separation of Copper from Tin.**—Weighed amounts of copper and tin were dissolved and the electrolyte was prepared according to the general directions given at the beginning of this paper. Special care was taken to avoid an excess of nitric acid, and to avoid heating the solution above  $75^{\circ}$ , or it was found impossible to recover all of the dissolved metals.

The copper was deposited by limiting the cathode potential to  $-0.40$  volt against the "normal calomel electrode." The cathode was weighed, replaced in the solution, two grams additional of hydroxylamine hydrochloride were added, and the tin was deposited in accordance with the directions given for depositing tin. The following results were obtained:

TABLE IV.

Copper.			Tin.		
Present.	Found.	Error. %.	Present.	Found.	Error. %.
0.5165	0.5165	0.00	0.6126	0.6147	+0.34
0.4502	0.4482	-0.42	0.3148	0.3162	+0.42
0.3334	0.3344	+0.30	0.2124	0.2120	-0.20
0.5002	0.5004	+0.04	0.5002	0.5008	+0.12
0.5002	0.5006	+0.08	0.5860	0.5858	-0.03

Some of our students secured excellent results when they limited the cathode potential to  $-0.50$  volt. (See also Section 2, second paragraph.) Qualitative tests were made to determine whether the separation was complete. The absence of tin in the copper deposit was shown by the

absence of a precipitate of stannic oxide when the copper deposit was dissolved in nitric acid. The absence of copper in the "residual" electrolyte was shown by the "ferrocyanide test." Finally, after the deposition of the tin, the solutions were treated with hydrogen sulfide to ascertain whether all the tin had been deposited; no discoloration of the solution was produced by the hydrogen sulfide.

**4. The Determination of Bismuth.**—In order to obtain a good deposit of bismuth out of an electrolyte which contained hydrochloric acid and hydroxylamine hydrochloride, it was necessary to limit the potential of the cathode against the "normal calomel electrode" to  $-0.25$  volt, or less, until most of the metal had been deposited and the current had been reduced to a very small fairly constant value. Then the applied voltage was raised gradually so that the residual current was not appreciably increased, and the electrolysis continued until the potential of the cathode against the calomel electrode attained the value  $-0.5$  volt. Then the current was interrupted.

"Analyzed" pure oxychloride of bismuth was employed for the following determinations. The samples were dissolved in 5 cc. hydrochloric acid, sp. gr. 1.2, and 2 g. of hydroxylamine hydrochloride were then added. The solution was diluted to 200 cc., heated to  $55-75^{\circ}$  and subjected to electrolysis in the manner stated before.

TABLE V.

BiOCl.	Bismuth.		Error. %.
	Present.	Found.	
0.4938	0.3958	0.3954	$-0.10$
0.4049	0.3245	0.3247	$+0.06$
0.3930	0.3150	0.3150	$-0.00$
0.4298	0.3445	0.3442	$-0.09$
0.4551	0.3648	0.3646	$-0.06$

**5. The Determination of Antimony.**—Several peculiar properties of antimony and its salts must be considered in connection with its electrolytic determination. If hydrogen is evolved during the electrodeposition of the metal, some of the latter will escape in the form of stibine. If the electrodeposition takes place below  $50^{\circ}$ , the impure "explosive" antimony is deposited;<sup>1</sup> while above  $70^{\circ}$  the tendency of the antimony chloride solutions to hydrolyze increases rapidly with increase of temperature, and antimony chloride will be lost by volatilization. Our electrolytic method was designed to avoid all these sources of error.

Weighed samples of antimonous oxide,  $Sb_2O_3$ , "Analyzed" were treated with 20 cc. of hydrochloric acid, sp. gr. 1.20 (more than is used for other metals—on account of the hydrolyzing tendency of the antimony), and with 2 g. of hydroxylamine hydrochloride. The resulting solution was

<sup>1</sup> *Z. physik. Chem.*, **52**, 129 (1905).

diluted to 200 cc. The dilution of any solution containing antimony chloride must always be made very quickly while stirring, in order to prevent hydrolysis. The electrolyte was heated to a temperature between 50 and 75° and deposited on copper-plated electrodes with a cathode potential of  $-0.30$  to  $-0.40$  volt against the normal calomel electrode until the current dropped to "zero." The following results were obtained

TABLE VI.

Time.	$Sb_2O_3$ .	Antimony.		Error. %.
		Present.	Found.	
15 min.....	0.6990	0.5825	0.5814	$-0.20$
10 min.....	0.4390	0.3658	0.3647	$-0.30$
10 min.....	0.5542	0.4618	0.4600	$-0.40$
8 min.....	0.2456	0.2047	0.2048	$+0.05$
15 min.....	0.4708	0.3923	0.3928	$+0.12$
5 min.....	0.4844	0.4038	0.4044	$+0.15$

**6. The Separation of Antimony (or Bismuth) from Tin.**—The sample was prepared as previously stated, except that 15 cc. of concentrated hydrochloric acid were employed (to prevent the hydrolysis of the antimony salts), and 4 g. hydroxylamine hydrochloride were added. The solution was diluted to 200 cc., heated to 50°, and electrolyzed with the cathode potential at  $-0.40$  volt until the current reached a constant minimum which indicated that the deposition of the antimony was complete.

TABLE VII.

Antimony		Error. %.	Tin.		Error. %.
Present.	Found.		Present.	Found.	
0.2107	0.2106	$-0.05$	0.2878	0.2886	$+0.29$
0.3443	0.3448	$+0.14$	0.3044	0.3032	$-0.40$
0.2757	0.2760	$+0.11$	0.5582	0.5562	$-0.35$
0.2580	0.2582	$+0.08$	0.3482	0.3484	$+0.06$
0.3180	0.3182	$+0.06$	0.3712	0.3706	$-0.16$
0.4457	0.4444	$-0.29$	0.4948	0.4926	$-0.44$
0.2105	0.2006	$+0.05$	0.2846	0.2838	$-0.29$
0.3945	0.3946	$+0.03$	0.6578	0.6580	$+0.03$

This is evidently to be preferred to the tedious gravimetric separation of these two metals.

Since bismuth may be deposited out of the same electrolytes at a potential slightly "less zincic" than that required for antimony, the separation of bismuth from tin can undoubtedly be effected under the same general conditions given for the determination of bismuth. As much of this metal as possible must be deposited while the cathode potential is limited to  $-0.25$  volt, or less, against the calomel electrode; then the applied voltage is to be raised, without increasing the residual current, until the cathode potential has attained the value  $-0.40$  volt.

**7. The Determination of Lead.**—Copper-plated electrodes were used for all lead deposits.

Weighed quantities of "Analyzed" lead chloride were dissolved in 200 cc. of hot water to which 10 cc. of concentrated hydrochloric acid had been added. The reducing agent was added and the solution electrolyzed while warm (60–70°) with a current of 1.5 amperes for 25 or 40 minutes. The "end point" was determined as with tin—by replacing the weighed electrode in the electrolyte, electrolyzing further, and weighing the electrode again. The solution was also treated with hydrogen sulfide to prove the absence of lead. The following results were obtained:

TABLE VIII.

Reducing agent employed.	Amount of lead chloride.	Lead.		Error. %
		Present.	Found.	
Oxalic acid.....	0.5912	0.4403	0.4396	—0.16
Oxalic acid.....	0.7292	0.5432	0.5430	—0.04
Hydroxylamine hydrochloride.....	0.8970	0.6681	0.6674	—0.10
	0.3292	0.2452	0.2456	+0.16
	0.3462	0.2579	0.2580	+0.04
	0.3746	0.2792	0.2790	—0.07
Formalin.....	0.2734	0.2036	0.2038	+0.10
	0.3282	0.2444	0.2438	+0.16
	0.3042	0.2265	0.2262	—0.13
	0.3036	0.2260	0.2258	—0.09

These results are more reliable than those obtained by depositing lead as a peroxide.<sup>1</sup> One remarkable feature of this deposition of lead is that formaldehyde may be employed while it cannot be employed in the deposition of tin. The difference may be due to the fact that the lead chloride, unlike stannous chloride, is not an active reducing agent.

### 8. The Simultaneous Deposition of Lead and Tin and Their Separation.

—The potentials at which tin and lead are deposited from acidified chloride solutions are so close together that an electrolytic separation is impossible. On this account, and because these metals alloy readily, they are deposited together under the same conditions under which either one is deposited; hence both together may be separated from other metals just as either one alone may be deposited. This leaves us merely the special problem of their separation.

When an alloy of tin and lead is treated with nitric acid, the insoluble stannic oxide adsorbs some of the lead salt; hence the separation is incomplete. It occurred to us that it might be possible to find a salt which would be adsorbed more readily than the lead nitrate, and which, if added to the mixture, would allow the lead salt to be released. When potassium nitrate is added to the nitric acid a complete separation of tin and lead is effected. The lead may be deposited as peroxide from one of the two separate portions thus obtained; and the tin may either be obtained by difference, or it may be determined by treating the insoluble stannic

<sup>1</sup> Sand, *Faraday Society*, 5, 210.



oxide with concentrated hydrochloric acid and hydroxylamine hydrochloride, and depositing the tin by electrolysis.

This separation was carried out according to two slightly different methods of procedure. In the first, the mixture of tin and lead was treated with nitric acid in the usual manner, the mixture was heated until all nitrous oxide fumes were expelled, diluted to 200 cc., boiled, stirred for ten minutes with the stirrer of the electrolytic apparatus and filtered. The impure precipitate was washed back into the beaker, 10 g. potassium nitrate were added, the mixture was boiled, stirred and filtered as above. The lead in the filtrate was determined by electrodeposition on the anode as lead dioxide. The stannic oxide was immediately treated with concentrated hydrochloric acid in presence of hydroxylamine hydrochloride, and the tin deposited from the resulting solution by our method.

TABLE IX.

Lead.			Error. %.	Tin.		Error. %.
Present.	PbO <sub>2</sub> .	Found.		Present.	Found.	
0.3886	0.4474	0.3874	-0.31	0.6644	0.6636	-0.12
0.5050	0.5828	0.5047	-0.06	0.7850	0.7846	-0.05
0.5546	0.6394	0.5537	-0.16	0.3452	0.3452	0.00

In the second method, the mixture of tin and lead was dissolved in 10 cc. of concentrated nitric acid in the presence of 10 g. of potassium nitrate dissolved in 40 cc. of water. The mixture was heated as before to expel the nitric oxide fumes, diluted to 200 cc., boiled, stirred for fifteen minutes with the stirring apparatus used for the deposition, cooled, filtered and washed. The tin and the lead were then determined as stated above.

TABLE X.

Lead.			Error. %.	Tin.		Error. %.
Present.	PbO <sub>2</sub> .	Found.		Present.	Found.	
0.4718	0.5462	0.4730	+0.25	0.4310	0.4310	0.00
0.4074	0.4710	0.4079	+0.12	0.4414	0.4422	+0.18
0.3052	0.3520	0.3048	-0.13	0.5126	0.5130	+0.08

In addition to the above quantitative separation, a qualitative test was made to show that none of the lead salt remained in the stannic oxide. The precipitate was dissolved in a mixture of concentrated hydrochloric acid and hydroxylamine hydrochloride, then diluted and treated with hydrogen sulfide, and the precipitate treated with yellow ammonium sulfide; it dissolved completely.

**9. The Separation of Tin from Cadmium.**—Mixtures containing known amounts of stannous and cadmium chlorides were prepared by measuring out portions of solutions of known concentrations of these salts. Sufficient hydrochloric acid was added to prevent hydrolysis, 2 g. of hydroxylamine hydrochloride were added, and the requisite amount of water to bring the volume to 200 cc. With the solution warmed to 70°, the tin was deposited

by limiting the current to 1.5 amperes until the cathode potential had attained the value  $-0.70$  volt against the "normal calomel electrode." Then the current was reduced in order to keep the cathode potential constant until the current attained a constant "residual" value. The tin was found to have been completely deposited. After weighing, the cathode was replaced, the applied electromotive force was raised until a current of one ampere passed (higher currents gave spongy deposits of cadmium), and this current was continued until a qualitative test showed the absence of cadmium. About forty to sixty minutes were required to complete the deposition of the cadmium.

TABLE XI.

Tin.		Error. %.	Cadmium.		Error. %.
Present.	Found.		Present.	Found.	
0.4710	0.4710	0.00	0.3010	0.3010	0.00
0.4710	0.4712	+0.05	0.3010	0.2994	-0.50
0.4710	0.4710	0.00	0.3040	0.3048	+0.26
0.4710	0.4700	-0.22	0.3010	0.3006	-0.13

No trial was made to separate lead, or lead and tin, from cadmium, but from our point of view no reason can be seen why the separation could not be accomplished in the same way as the separation of tin from cadmium.

**10. The Separation of Copper from Antimony by Means of Hydrochloric-Tartaric Acid Electrolytes.**—Copper and antimony were dissolved as usual in hydrochloric acid with the minimum amount of nitric acid. Then 8-10 g. of tartaric acid were added, the mixture was diluted and electrolyzed. The electrolyte was kept cool, not to exceed  $25^{\circ}$ , because at higher temperatures greater potentials are required to deposit the copper completely out of acidified tartrate electrolytes, and the separation of copper from antimony becomes impossible. A current of two amperes was allowed to pass until the "observed cathode potential" had attained the value  $-0.50$  volt; then the current was reduced so as to keep the "cathode potential" constant at  $-0.50$ ; when the current had become practically zero, the applied voltage was kept constant until the cathode potential rose to  $-0.65$  volt; then the experiment was terminated. Of course, this separation can be made with lower potentials, but not as rapidly.

Copper.		Error. %.	Copper.		Error. %.
Present.	Found.		Present.	Found.	
0.3596	0.3604	+0.22	0.3444	0.3442	-0.06
0.4424	0.4432	+0.18	0.4582	0.4588	+0.13
0.4782	0.4778	-0.08	0.5790	0.5788	-0.03

As the deposit was excellent in color and the remaining electrolyte gave no indication of copper with the ferrocyanide test, the separation was considered to be quantitative. No reliable method is known for

depositing the antimony out of tartrate solution; we found that only a portion of the antimony could be deposited.

**11. The Separation of Copper and Antimony from Lead by the General Method and the Separation of Copper from Antimony by means of Nitric-Tartaric Acid Electrolytes.**—In this procedure we separated copper and antimony from lead by depositing the first-mentioned two metals together. We did not make the corresponding separation of copper and antimony together from tin because the similarity in the properties of these metals indicates that this separation can be carried out by the method given under this heading—an idea that is confirmed by the results given in Section 13.

Weighed quantities of copper, antimony and lead were dissolved in the usual manner, except that 20 cc. of concentrated hydrochloric acid were used in place of 10 cc. to prevent hydrolysis of the antimony salts. To this mixture, 2 g. hydrazine hydrochloride were added, the mixture was diluted slightly and heated slowly to 60° with constant stirring. There was an evolution of gas, which was probably due to the action of the hydrazine on the nitrous oxides. Then the solution was diluted while hot, to 200 cc. and electrolyzed with a copper plated cathode. The copper and antimony were deposited together by limiting the cathode potential to  $-0.40$  volt against the normal calomel electrode until the current fell to a tenth of an ampere; then the applied voltage was kept constant until the cathode potential against the auxiliary electrode was  $-0.50$ . The electrode with the deposit of copper and antimony was weighed and the deposit was dissolved in diluted nitric acid in the presence of 10 g. of tartaric acid. Then the copper was deposited with the cathode potential limited to  $-0.30$  volt, and the temperature limited to 20°. The copper deposit had an excellent appearance. The weight of the antimony was obtained by subtracting the weight of the second deposit from the first. The lead, still in the first electrolyte, was deposited on a copper plated cathode.

TABLE XII.

Copper			Antimony.			Lead.		
Present.	Found.	Error. %.	Present.	Found.	Error. %.	Present.	Found.	Error. %.
0.5516	0.5516	0.00	0.5726	0.5730	$-0.07$	Not determined		
0.3040	0.3050	$+0.13$	0.3956	0.3948	$-0.20$	0.4250	0.4258	$+0.18$
0.4372	0.4378	$+0.13$	0.4684	0.4674	$-0.10$	0.6026	0.6012	$-0.22$
0.4130	0.4120	$-0.12$	0.4836	0.4838	$+0.04$	0.6034	0.6039	$+0.07$
0.3382	0.3382	0.00	0.3906	0.3900	$-0.15$	0.4762	0.4772	$+0.21$

**12. The Simultaneous Deposition of Antimony, Bismuth and Copper out of Electrolytes Containing These Metals and Tin.**—The first three were separated from tin by depositing them together according to the directions given for the determination of bismuth, Section 4.

Bi + Cu + Sb.		Error. %.
Present.	Found.	
1.0930	1.0922	-0.08
0.9370	0.9380	+0.11

The separation of these metals from solutions containing both lead and tin has been accomplished by the same method as that here employed (see Section 13).

In the separation of antimony, bismuth and copper from tin, it was noted that bismuth always came out first; in other words, bismuth is deposited from acid chloride solutions at a lower "cathode potential" than either copper or antimony, hence should be placed lower in the electro-motive series than copper, while antimony should be placed above copper. However, the deposition potential of bismuth is so near to that of copper that it was found impossible to separate it from the latter out of these electrolytes.

**13. The Simultaneous Deposition of Copper, Bismuth and Antimony out of Electrolytes Containing These and also Lead and Tin.**—Samples of weighed quantities of copper, of bismuth oxychloride, and of antimony oxide, and unweighed quantities of lead and tin were dissolved according to the usual procedure. When lead chloride was present in relatively large amounts, the crystals of this substance were removed by filtration. The copper, bismuth and antimony were deposited by the method given for the determination of bismuth, except that it was found necessary to limit the cathode potential to  $-0.20$  volt against the normal calomel electrode in order to obtain good deposits. As in the determination of bismuth, finally the cathode potential was allowed to "rise" to  $-0.35$  volt. The results obtained were as follows:

TABLE XIII.

Cu + Sb + Bi present.	Cu + Sb + Bi found.	Error. %.	Cu + Sb + Bi. present.	Cu + Sb + Bi found.	Error. %.
0.7783	0.7787	+0.05	0.7805	0.7811	+0.09
0.7587	0.7589	+0.03	0.7338	0.7344	+0.09
0.7199	0.7189	-0.14	0.7754	0.7754	+0.00
0.5194	0.5188	-0.11	0.8077	0.8085	+0.10
0.6913	0.6916	+0.04			

From 45 to 60 minutes were required for the separation.

The bismuth was apparently deposited first, and at the same time the solution lost the blue-green color of the cupric ion; then a purple grape-colored alloy of copper and antimony began to be deposited, and the cathode potential fell, it being necessary to again raise the current; finally, a grayish black deposit of apparently pure antimony covered the electrode. Sometimes it happened that there were alternate depositions of the alloy and of the antimony, but the deposition of the alloy was heralded by a "drop" in the cathode potential.

**14. The Separation of Bismuth from Antimony.**—Definite quantities of bismuth oxychloride and of antimony oxide were weighed out into the same electrolyzing beaker, dissolved in 5–7 cc. of hydrochloric acid (sp. gr. 1.2), and the resulting solution was diluted up to 150 or 175 cc.; 4–8 g. of potassium tartrate were added, and the solution was boiled for several minutes. Two grams of hydroxylamine hydrochloride were added, the temperature was raised to 70°, and the solution was electrolyzed with the cathode potential limited to 0.20 volt against the normal calomel electrode. Since bismuth “burns” very easily while being deposited, it was necessary to watch the cathode potential carefully and to prevent it from exceeding the limit of —0.20 volt. The main electrolyzing current was reduced continuously until there was no further tendency for the cathode potential to rise. Long before this state of affairs was attained, the electrolyzing current was practically zero—yet it was necessary to continue electrolysis and to decrease the applied voltage until the cathode potential showed no disposition to rise. This required 20–30 minutes. By this procedure, bismuth was deposited quantitatively and entirely free from any antimony. The results obtained were as follows:

Sb <sub>2</sub> O <sub>3</sub> .	Bismuth.		Error. %.
	Present.	Found.	
0.20	0.3160	0.3150	—0.31
0.20	0.3288	0.3284	—0.12
0.30	0.3888	0.3888	±0.00
0.40	0.3451	0.3446	—0.20

The deposits were all in excellent condition.

**15. The Separation of Copper and Bismuth from Antimony.**—As the easiest method of removing a deposit containing antimony from the electrode is with nitric and tartaric acids, an attempt was first made to deposit copper and bismuth simultaneously from a nitric-tartaric acid electrolyte which contained these metals and antimony. A triple alloy obtained as stated in Section 13 was dissolved in the minimum amount of nitric acid and 5–6 g. of tartaric acid. The solution was diluted to 150 or 175 cc. and electrolyzed. The temperature was kept at 25° or below, as in the separation of copper from antimony in the same electrolyte (Section 11). At the beginning of the deposition, the cathode potential was about —0.10 volt against the normal calomel electrode, but toward the end it was allowed to rise to —0.20 volt. Copper was the first metal to be deposited; this order was the opposite of that observed in chloride electrolytes. The solution was not free of copper when the color of the cupric ion had disappeared, but a considerable amount of copper was still present in the cuprous state while bismuth was being deposited. It happened quite often that there were alternate depositions of bismuth and of copper long after all color had disappeared. On ac-

count of the solubility of the copper in the nitric acid, siphon washing was resorted to in most instances. Some of the results which we obtained are as follows:

TABLE XIV.

Sb present.	Cu + Bi present.	Cu + Bi found.	Error. %.
0.20	0.5368	0.5347	—0.40
0.40	0.4794	0.4814	+0.40
0.20	0.4607	0.4629	+0.45
0.30	0.5303	0.5298	—0.10
0.20	0.5005	0.5034	+0.58
0.20	0.4594	0.4608	+0.30

The end point of the determination was indistinct, and the high results show that, in the deposition of the last traces of copper, antimony in small amounts was probably deposited with it. The results were not considered satisfactory.

We next tried the separation in acidified chloride electrolytes. A triple alloy obtained as in Section 12 or 13 was dissolved from the platinum electrode as follows: 25–30 cc. of 1 : 3 hydrochloric acid were warmed up to about 60° in an electrolyzing beaker, the electrode was put in, and then a very few drops of conc. nitric acid were added, care being taken to use the least amount necessary to start a moderate attack on the alloy. When all of the sample had been dissolved, crushed ice was added sufficient to lower the temperature to 10° or below; then about 5 g. of tartaric acid were added. Electrolysis was carried out at this low temperature; at higher temperatures there appears to be an extensive formation of a complex tartrate-copper ion, from which the copper cannot be recovered. From time to time, small lumps of ice were added to the electrolyte to keep its temperature down.

The cathode potential was limited at the beginning to —0.15 or —0.20 volt against the normal calomel electrode, but to deposit the last of the copper it was allowed to rise to —0.40 volt. Hydrogen began to be evolved soon after, and the experiment was terminated. From 90 to 120 minutes was the time required for the deposition of the samples in the table below.

TABLE XV.

Sb present.	Copper and bismuth.		Error. %.
	Present.	Found.	
0.23	0.5552	0.5558	+0.10
0.30	0.6750	0.6748	—0.03
0.30	0.7156	0.7162	+0.08
0.20	0.6752	0.6746	—0.09

**16. The Separation of Bismuth from Copper.**—Bismuth cannot be separated from copper by the "graded potential" method, but either bismuth or copper can be separated from antimony. When all three metals

are present, the first procedure to suggest itself is to remove either bismuth or copper from the solution, and to separate the other two by one of the methods given above. Hence we made a complete study of Moser's method<sup>1</sup> for precipitating bismuth phosphate in order to ascertain if bismuth could thus be removed quantitatively from solutions of these three metals.

Pure deposits of bismuth were prepared according to the directions in Section 4. The deposit was dissolved in the least possible amount of nitric acid (3-5 cc.). Tartaric acid was also used in order to reproduce the conditions which would be obtained in an actual separation of bismuth from copper and antimony. A slight excess of a 10% solution of ammonium phosphate was added to the hot solution. After a short period of digestion, the precipitate was transferred to a filter paper, and was washed with a decinormal solution of nitric acid to which a few cubic centimeters of the precipitant had been added. The bismuth was dissolved in hydrochloric acid and deposited according to the method given above for its determination. This was done first, with bismuth alone in the solution, then with copper present, and finally in the presence of antimony. The following results were obtained:

TABLE XVI.

Cu.	Sb.	Tartaric acid.	Bismuth.		Error. %.
			Present.	Found.	
None	None	5 g.	0.9172	0.9140	-0.34
None	None	5 g.	0.6860	0.6859	-0.01
None	None	5 g.	0.8912	0.8912	±0.00
0.25	None	5 g.	0.5678	0.5666	-0.21
0.12	None	5 g.	0.6066	0.6042	-0.39
None	0.24	5 g.	0.6068	0.6233	+2.7
None	0.16	5 g.	0.6068	0.6200	+2.1

These results show that bismuth phosphate is precipitated quantitatively and in pure form when it is present alone in the electrolyte or together with copper, but not when it is together with antimony. On this account the order of procedure above suggested had to be changed to the following:

The copper and bismuth were separated from antimony by the method given in Section 15, and then the bismuth was separated from the copper by the method given above. The following results were obtained:

TABLE XVII.

Cu.	Bismuth.		Error. %.
	Present.	Found.	
0.26	0.5128	0.5118	-0.20
0.37	0.2589	0.2580	-0.40
0.25	0.2312	0.2318	+0.26

AUSTIN, TEXAS.

<sup>1</sup> *Z. anal. Chem.*, 45, 19 (1906).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TEXAS.]

## THE ELECTROANALYSIS OF SILVER WITH SOLUTIONS OF SILVER CHLORIDE IN AMMONIA.

By E. P. SCHOCH AND F. M. CRAWFORD.

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A method for the quantitative electrodeposition of silver out of solutions of silver chloride in ammonia has not been published so far, but the use of this electrolyte appears to be very desirable, because it is likely to yield pure deposits while the cyanide electrolyte—the only other solvent for silver chloride heretofore employed in electroanalysis—produces impure deposits.

We have found that approximately 99.6% of the silver in an ammoniacal solution of silver chloride can be deposited by electrolysis in good form. It is merely necessary to increase the conductivity of the solution by adding enough of an ammonium salt (ammonium chloride) to the solution, and to electrolyze with a small current density at the ordinary temperature.

In order to deposit the small remnant of silver left in the electrolyte, the ammonia is neutralized with a slight excess of hydrochloric acid, and a weak reducing agent (oxalic acid) is added: from this electrolyte the remainder of the silver may be deposited completely and in good form. The presence of nitrates (or of nitric acid in the original mixture) does not affect the result.

Care must be taken to clean the platinum cathode thoroughly, to keep the current density small in order to avoid "burning" the deposit, and to wash and handle the electrode with the deposit *gently* to avoid knocking off the deposit. With a little care on these points, the determination is easily carried out and gives satisfactory results, as is shown below.

The following determinations were made with the electrolytic apparatus described in the foregoing paper by E. P. Schoch and D. J. Brown: Samples of pure sheet silver were dissolved in concentrated nitric acid and the silver was precipitated with a slight excess of hydrochloric acid. With several of the samples, the silver chloride was filtered, washed and dissolved in a slight excess of concentrated ammonia; and with others the original mixture (containing the excess of nitric acid) was treated with ammonia. About 20 g. of ammonium chloride and enough water were added to each mixture to bring the volume to approximately 150 cc. (enough to cover the electrodes), and the solutions were electrolyzed at room temperature with an initial amperage of 0.35 amp. (which with our apparatus required 1.1 volts between the electrodes). This voltage was kept constant until the current had dropped to zero: care had to be taken to reduce the current promptly while the metal was being deposited because the maximum allowable current density (which



cannot be exceeded without obtaining a dark and loosely adherent deposit) rapidly becomes less as the silver content of the solution becomes less. When the amperage had become practically zero, the voltage was allowed to rise gradually to 1.3-1.4 volts and electrolysis continued until a total of 25-30 minutes had elapsed. This period must necessarily be larger if the quantity of silver to be deposited is greater than that which we used.

Then, without disturbing the apparatus, about 3 g. of oxalic acid crystals were added to the solution, and enough concentrated hydrochloric acid to make the solution faintly acid to litmus paper. Without increasing the applied voltage, electrolysis was continued for about 20 minutes. Then the experiment was terminated, and the electrodes were washed and dried in the manner described in the preceding paper. The following results were obtained:

TABLE I.—DEPOSITION OF SILVER.

Silver present. G.	Found. G.	Error.	
		G.	%.
0.1595	0.1591	-0.0004	-0.25
0.5887	0.5886	-0.0001	-0.02
0.3704	0.3699	0.0005	+0.14
0.2958	0.2956	0.0002	+0.07
0.4030	0.4027	0.0003	+0.07
0.5139	0.5139	0.0000	0.0
0.2551	0.2551	0.0000	0.0

AUSTIN, TEXAS.

[CONTRIBUTION FROM THE DEPARTMENT OF SOIL BIOLOGY OF THE OHIO AGRICULTURAL EXPERIMENT STATION.]

## TITRAMETRIC DETERMINATION OF NITRITES.

By B. S. DAVISSON.

Received May 10, 1916.

The frequent necessity of determining nitrites in the investigation of the physiology of the process of nitrification, reveals the need of a satisfactory titrametric method for such determination.

Nitrite determinations are usually made by colorimetric methods. It would be more desirous to make nitrite determinations titrametrically and avoid the errors which are so often introduced in colorimetric methods, namely, errors of dilution, eye fatigue, color comparison and the individual error of the worker.

### Historical.

The reaction of nitrous acid with hydriodic acid is well known:  $2\text{HI} + 2\text{HNO}_2 \rightarrow 2\text{H}_2\text{O} + 2\text{NO} + \text{I}_2$ . Since this reaction proceeds quantitatively, titration of the liberated iodine with standard thiosulfate has been used as a titrametric method for determining nitrous nitrogen. The

nitric oxide evolved in the reaction passes readily back into nitrous acid in contact with air and water and will oxidize more hydriodic acid, unless air is excluded from the titrating flask.

Winkler<sup>1</sup> has worked out a time method for determining small amounts, less than  $\frac{1}{3}$  mg., of nitrites in waters. The method depends upon the reactions taking place in the presence of oxygen. After the solution has stood for some time in contact with the acid, iodide and starch solution, the liberated iodine is titrated with 0.005 *N* sodium thiosulfate. The author compiled a table showing the milligrams of  $N_2O_3$  in a liter of the solution for a given quantity of the thiosulfate. The table is compiled for periods of 3, 6 and 24 hours. The author recommends the 24-hour period as giving the most satisfactory results.

Winkler<sup>2</sup> proposed a second method for determining nitrites when the quantity present is greater than  $\frac{1}{3}$  mg.  $N_2O_3$ . He used  $KHCO_3$  as a source of  $CO_2$  to expel the air from the titration flask. After ten minutes the iodine is titrated.

Sutton<sup>3</sup> outlines the Dustan and Dymond method in which the air is expelled from the flask by boiling the solution of acid, starch and potassium iodide and closing off the flask with a pinchcock, thus creating a vacuum when the solution cools. The nitrite solution is then introduced and the liberated iodine titrated with standard thiosulfate.

Wiley<sup>4</sup> outlines the Chabier method for the quantitative determination of nitrites. The air is expelled from the titrating flask by carbon dioxide or illuminating gas. The reaction of the acid, potassium iodide, and starch solution is allowed to take place after the air is expelled, and the liberated iodine is titrated with standard thiosulfate.

### Experimental.

The two methods proposed by Winkler were investigated. The procedure was the same as that employed by Winkler.

The results obtained by the first method were too high in practically all of the determinations made. No satisfactory results were obtained from a great number of trials.

Since this method depends upon the reaction taking place in the presence of oxygen, it seems probable that one might pass a slow current of air through the solution and accomplish the desired oxidation in a very short time. This, of course, would require the formulation of another table to be used in connection with the method.

Winkler's second method gave no better results than those obtained by his time method. Trouble was experienced in getting all the oxygen out

<sup>1</sup> *Z. Nahrungs und Genussmittel*, 29 (1915).

<sup>2</sup> *Loc. cit.*

<sup>3</sup> "Volumetric Analysis," 10th Ed., p. 287.

<sup>4</sup> "Princip. and Pract. of Agric. Analysis," 2nd Ed., Vol. II, p. 474.

of the flask. Five grams of  $\text{KHCO}_3$  as recommended by Winkler, was not sufficient. It is necessary that no air enter the flask during titration and this can be accomplished only when a rapid current of  $\text{CO}_2$  passes out of the solution. The results obtained with this method were in every case too high.

The work was carried no further on the method proposed by Winkler. The method cannot be used where large quantities of nitrites are present. Since the amount of nitrite which we wish to determine may be large or very small, it was thought better to develop a method which can be used with both large and small quantities of nitrites.

The Dustan and Dymond method was next used. Special burets were prepared for the standard thiosulfate and nitrite solutions. The burets were connected with the flask through a two-way stopcock and all air was excluded in making the connections. It was found almost impossible to prevent the leakage of air into the flasks. Air was drawn in about the rubber stoppers, though they appeared to be very tight. A method simpler in manipulation and still capable of a high degree of accuracy was sought.

Since the iodometric method of determining nitrite nitrogen depends upon the determinations being carried on in the absence of oxygen, it would be better to expel the air by means of some inactive gas and make the titrations while a slow current of this gas is passing through the flask. The Chabier method with some improvements should give trustworthy results for fractions of a milligram. The starch iodide reaction is extremely delicate and if careful precautions are taken to expel all air one should get excellent results.

Either natural gas or commercial carbon dioxide may be used to expel the air from the titration flask. These gases were each found to be effective. The low cost and ease of handling of carbon dioxide makes it easily available for this purpose and it is used in this laboratory. It requires no further purification and can be passed directly from the cylinder through the flask.

A special aeration flask was used, as shown in Fig. 1. It is a large-mouthed Erlenmeyer flask with an aerating tube sealed through the side and extending to the bottom of the flask where an arm is bent parallel to the flask bottom. The tube has several openings on either side to permit a rapid escape of gas. Such an arrangement gives good distribution of the gas and enables one to get immediate expulsion of the air. The flask is closed with a rubber stopper bearing an outlet for the gas, a separatory funnel for introducing the acid, a buret for the standard thiosulfate and a second

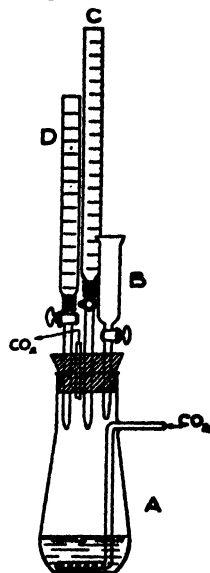


Fig. 1.

buret to carry a standard nitrite solution to be used in case the end point is overstepped. A stand with a white porcelain base is used with the apparatus.

**Procedure.**—Bring the solution to be tested into flask A and make to a volume of about 150 cc. Add 0.5 g. of pure KI and 2 cc. of a starch solution. Insert the stopper and allow a slow current of  $\text{CO}_2$  to pass through the flask for three minutes. Reduce the current of  $\text{CO}_2$  to a few bubbles, just sufficient to prevent any diffusion of air into the flask during titration. Add about 10 cc. of a 15% solution of  $\text{H}_2\text{SO}_4$ , and allow the solution to react for a short time before titrating the liberated iodine with thiosulfate.

The results reported in this paper were obtained upon a standard nitrite solution. The nitrite solution was prepared from silver nitrite, the silver being precipitated from the solution with sodium chloride. The solution was filtered, the precipitate washed free of nitrites and the solution then made to a definite volume. Standard thiosulfate of 0.1 N, 0.05 N, 0.02 N and 0.005 N strengths were used for making titrations.

Table I contains results obtained where variable quantities of a standard nitrite solution were used. Twentieth normal thiosulfate was used in making the titrations.

TABLE I.

Nitrite solution. Cc.	$\text{Na}_2\text{S}_2\text{O}_4$ . Cc.	Nitrogen taken. Mg.	Nitrogen found. Mg.	Error.
25.06	12.07	8.51	8.47	—0.04
22.86	11.05	7.77	7.74	—0.03
25.35	12.22	8.61	8.56	+0.05
22.84	11.05	7.76	7.74	—0.02
18.20	8.86	6.18	6.20	+0.02
18.05	8.85	6.13	6.19	+0.06
17.93	8.71	6.09	6.10	+0.01
18.59	9.03	6.32	6.33	+0.01
20.28	9.90	6.89	6.93	+0.04

Two series were carried out with solutions containing 15.1 and 2.01 mg. of nitrogen as nitrite, respectively.

TABLE II.

No.	Cc. 0.1 N $\text{Na}_2\text{S}_2\text{O}_4$ .	Nitrogen. Mg.	Cc. 0.02 N $\text{Na}_2\text{S}_2\text{O}_4$ .	Nitrogen. Mg.
1.....	10.77	15.08	7.35	2.06
2.....	10.82	15.14	7.26	2.03
3.....	10.86	15.20	7.26	2.03
4.....	10.86	15.20	7.20	2.01
5.....	10.77	15.08	7.17	2.00
6.....	10.82	15.14	7.08	1.98
7.....	10.74	15.03	7.26	2.03
Theoretical.....	...	15.10	..	2.01

The method should give accurate results in the presence of organic matter if it is to be used in the study of the physiology of nitrification.

The effect of organic matter was next studied. Determinations were made in the presence of soil extract which contained considerable organic matter. Fifty cc. of a standard nitrite solution were added to 50 cc. of a soil extract and the nitrite was determined. Nitrites were determined separately on 50-cc. portions of the soil extract and the proper correction, 0.448 mg., was made.

TABLE III.—EFFECT OF ORGANIC MATTER ON NITRITE DETERMINATION. AMOUNT TAKEN, 10 MG. OF NITROGEN.

Cc. 0.1 <i>N</i> <i>Na</i> <sub>2</sub> <i>S</i> <sub>2</sub> <i>O</i> <sub>3</sub> .	Nitrogen found. Mg.	Nitrogen recovered. Mg.	Cc. 0.1 <i>N</i> <i>Na</i> <sub>2</sub> <i>S</i> <sub>2</sub> <i>O</i> <sub>3</sub> .	Nitrogen found. Mg.	Nitrogen recovered. Mg.
7.46	10.45	10.00	7.46	10.45	10.00
7.47	10.46	10.02	7.50	10.50	10.05
7.48	10.47	10.03	7.50	10.50	10.05
7.48	10.47	10.03	7.47	10.46	10.00

The organic matter of the extract does not affect the results very materially. In extreme conditions, however, the nitrites may be removed from a second sample by boiling with acetic acid, and the magnitude of the action due to organic matter determined by means of a blank titration.

Small quantities of nitrites may be determined in the open flask while a current of CO<sub>2</sub> is passing through the solution. Table III contains the results of such determinations. For very small quantities of nitrites 0.005 *N* thiosulfate is used.

TABLE IV.—AMOUNT TAKEN, 0.012 MG. NITROGEN.

Cc. 0.005 <i>N</i> <i>Na</i> <sub>2</sub> <i>S</i> <sub>2</sub> <i>O</i> <sub>3</sub> .	Mg. nitrogen.	Cc. 0.005 <i>N</i> <i>Na</i> <sub>2</sub> <i>S</i> <sub>2</sub> <i>O</i> <sub>3</sub> .	Mg. nitrogen.
0.19	0.013	0.18	0.012
0.16	0.011	0.17	0.012
0.14	0.009	0.18	0.012
0.19	0.013	0.16	0.011
0.19	0.013		

The results reported in this paper show clearly that nitrous nitrogen can be determined titrimetrically when care is taken to expel the air from the titration flask with some gas which will not affect the determination.

The author takes this opportunity to thank Mr. J. J. Kennedy and Dr. E. R. Allen for their assistance in carrying on this work.

WOOSTER, OHIO.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES, THE OHIO STATE UNIVERSITY.]

## SODIUM PYROGALLATE AS A REAGENT FOR THE DETERMINATION OF OXYGEN.

By J. W. SHIPLEY.

Received June 21, 1916.

TOPICAL OUTLINE.—Introduction and Historical. Reagents. Apparatus. Range of Concentrations. Specific Absorption of Reagents. Comparison with Potassium Pyrogallate. Volume of Oxygen Absorbed before Rate of Absorption Dropped to Four-minute Limit. Rate of Absorption. Temperature Coefficient. Relation of

Oxygen Absorbed to Amount of Pyrogallol. The Formation of Carbon Monoxide. Rate of Absorption in Various Pipets. Choice of Reagents for Gas Analysis. The Use of Ammonium and Barium Pyrogallate. Summary.

### Introduction and Historical.

The purpose of this research was to determine whether sodium pyrogallate might not be substituted for potassium pyrogallate in the absorption of oxygen from gaseous mixtures.

The evidence from the chemical literature available indicated that no one as yet had made a systematic study of the use of sodium pyrogallate in this connection and that chemists had on very doubtful evidence indeed discarded this reagent in favor of the more expensive potassium salt. Particularly at this time when circumstances have made it almost impossible to obtain the latter foreign product in any quantity did it seem desirable to determine whether the home product might not be as serviceable.

Potassium hydroxide is at present universally used in the preparation of alkaline pyrogallate for the absorption of oxygen. All text-books on gas analysis recommend its use and many researches have been carried out to determine the best proportion of alkali, pyrogallate and water to use in the preparation of the reagent. The best conditions for obtaining the most efficient absorption of oxygen by means of this reagent was the subject of a recent exhaustive research by R. P. Anderson.<sup>1</sup> Anderson made one determination with sodium pyrogallate in place of potassium pyrogallate, obtaining complete absorption only after twelve minutes' shaking. From this he concludes that such a reagent would scarcely be satisfactory for general use as an absorbent for oxygen.

Weyl and Goth<sup>2</sup> carried out a series of experiments, the results of which tended to indicate that sodium hydroxide might be better than potassium hydroxide in the preparation of this reagent.

Berthelot<sup>3</sup> found that the relative absorbing capacity of sodium and potassium pyrogallate was practically equivalent when the solution contained alkali in the proportion of three parts of alkali to one of pyrogallol. Dilution affected the rate of absorption and the evolution of carbon monoxide but the total absorbing power was not affected until the ratio between pyrogallol and alkali used dropped below 1 : 1. At 1-2 KOH to 1 of pyrogallol the amount of oxygen absorbed was reduced to one-half of that absorbed when the ratio was 3 : 1, respectively.

Lewes<sup>4</sup> prepared a reagent by dissolving 10 g. of pyrogallol in 150 cc. of 20% sodium hydroxide. Such a solution required twenty minutes for the complete absorption of oxygen and could not be used more than three

<sup>1</sup> Anderson, *J. Ind. Eng. Chem.*, 7, 587 (1915).

<sup>2</sup> Weyl and Goth, *Ber.*, 14, 2659 (1881).

<sup>3</sup> Berthelot, *Ann. Chem. et Phys.*, 77, 294 (1898).

<sup>4</sup> Lewes, *J. Soc. Chem. Ind.*, 10, 407 (1891).

or four times, since carbon monoxide was generated after a certain proportion of oxygen had been absorbed. Had Lewes gone further and used more concentrated solutions with respect to both alkali and pyrogallol he would have found the rate of absorption of oxygen much greater and would not have found any appreciable quantity of carbon monoxide.

The experimental work of Weyl and Goth at relatively low concentrations and of Berthelot at high concentrations indicated that sodium hydroxide might well have been considered in the preparation of alkaline pyrogallate. Chemists<sup>1</sup> have, however, in this as in many parallel cases, accepted the preference for a potassium compound without investigating fully the possible substitution of the cheaper sodium salt.

The results of a few preliminary determinations covering several different concentrations indicated clearly that the absorption of oxygen by sodium pyrogallate was sufficiently rapid to warrant a more extensive investigation. Moreover, no carbon monoxide appeared to be evolved from any of the concentrations used. Accordingly, apparatus and reagents were prepared for determining the best conditions and concentrations of sodium pyrogallate for the absorption of oxygen from gaseous mixtures.

**Reagents.**—Pyrogalllic acid was secured from the 1-pound can product prepared by a reputable firm.

Sodium hydroxide solution was prepared by dissolving electrolytic, pure stick sodium hydroxide in an equal weight of water. The alkali content of this solution was determined by diluting 10.0 cc. to a liter and titrating an aliquot portion against standard acid. Thus 10.0 cc. were found to contain 7.36 grams of sodium hydroxide or about 49.1%. This solution will be referred to as the stock solution.

Oxygen was prepared from the reaction between sodium peroxide and water. The preparation contained 95% of the gas.

**Apparatus.**—Fig. 1 illustrates in detail a special pipet outwardly resembling the Richard's form and inwardly that of the Orsat model.

Such a double pipet was found to be very efficient. It is com-

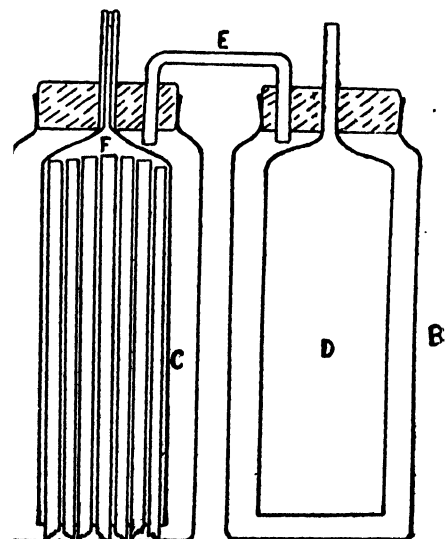


Fig. 1.

<sup>1</sup> Withrow, *J. Ind. Eng. Chem.*, 8, 486 (1916).

pact, stable, easy to construct or repair, not at all fragile and very convenient for filling or cleaning. The small glass tubes provide a very large absorbing surface and since no shaking is necessary the disadvantage arising from foaming when viscous solutions are used is entirely obviated.

This pipet was used in making the absorptions tabulated in Table I.

**A Simple Pipet.**—In determining the specific absorption of various alkaline pyrogallate solutions it was necessary to have a simple pipet and that depicted in Fig. 2 was found to give very satisfactory results. This pipet resembled in principle that described in Fig. 1.

A glass tube 6 mm. in diameter was sealed to the lower extremity and to this was attached a levelling bulb filled with mercury. A three-way capillary stopcock, C, Fig. 2, was sealed to the upper end of the pipet;

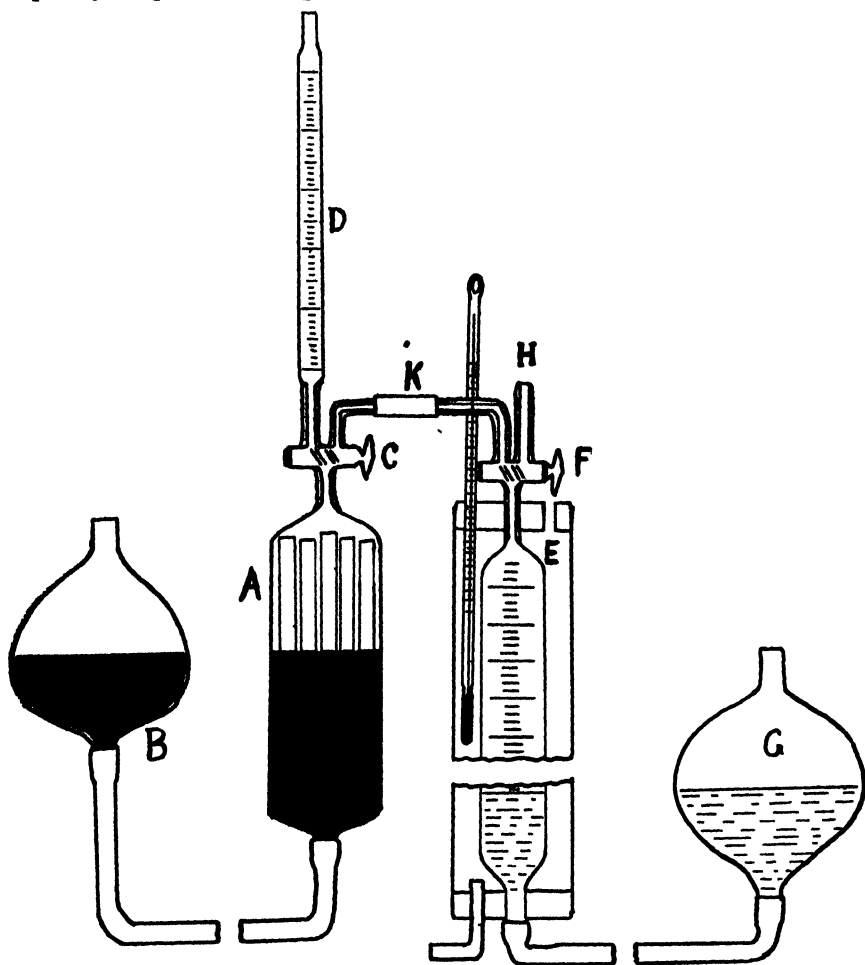


Fig. 2.



one arm led to the gas buret while to the other was sealed a 5 cc. pipet graduated in tenths. The gas buret was likewise provided with a three-way capillary stopcock, F, one arm being connected at K by pressure tubing with the corresponding arm of the absorption pipet, while the other, H, permitted the filling of the buret with air or with oxygen from the oxygen tank.

The carbon monoxide absorptions were made in the ordinary pipet of the Orsat apparatus.

**Range of Concentrations.**—A series of determinations was made for the purpose of finding out the range of concentration over which the rate of absorption was sufficiently rapid for the purpose in question. A weighed portion of pyrogalllic acid was placed directly into the pipet, Fig. 1, followed by a few cubic centimeters of water to prevent caking when the alkali solution was added. Depreciation of the reagent through contact with the air was obviated by filling the pipet with illuminating gas before adding the alkali.

The results collected in Table I represent the average of a number of determinations for each solution carried out by passing 50.0 cc. portions of air back and forth over the reagent three times in four minutes.

TABLE I.  
Time of Absorption of Oxygen by Sodium Pyrogallate.

	Composition of reagents in grams.			Time for complete absorption of oxygen from 50.0 cc. air.
	Pyrogallol.	NaOH.	H <sub>2</sub> O.	
1.....	10.0	110.4	114.3	Incomplete in 15 min.
2.....	15.0	117.8	131.9	4 minutes
3.....	20.0	73.6	96.2	2 minutes
4.....	20.0	73.6	106.2	2 minutes
5.....	20.0	73.6	156.2	4 minutes
6.....	20.0	73.6	206.2	Incomplete in 1 hr.
7.....	10.0	92.0	105.2	4 minutes
8.....	10.0	92.0	155.4	4 minutes
9.....	10.0	92.0	205.2	4 minutes
10.....	10.0	92.0	255.2	7 minutes

**Specific Absorption of Reagents.**—Since complete and rapid absorption of the oxygen over a considerable range in concentration was secured, the determinations of the specific absorption of the reagent for various concentrations was next carried out. This was done in the pipet already described in Fig. 2. The reagent with predetermined proportions of alkali, acid, and water was always prepared in a small dropping funnel. The required weight of pyrogalllic acid together with from one to four cubic centimeters of water—to prevent caking—was placed in the funnel and the air swept out with illuminating gas, by connecting the funnel in series with a Bunsen burner. The lighted burner disposed of the excess gas. Ten cubic centimeters of alkali from the stock solution were

next run in from a pipet and the funnel stoppered. The stem of the funnel was also provided with a stopper to prevent the gas from being displaced by air. The mixing of the alkali and pyrogallol was always accompanied by a considerable rise in temperature, but this apparently had no deleterious effect upon the reagent.

After cooling, five cubic centimeters of the reagent were transferred to the graduated pipet of the absorption apparatus, care being exercised to prevent any contact whatsoever with the air. The absorptions were carried out with 1.5 cc. portions of the reagent measured into the pipet by means of the graduate. Oxygen in measured volumes was introduced through the gas buret and passed to and fro between the pipet and buret until the rate of absorption had dropped to one cubic centimeter per ten minutes. To have waited for complete exhaustion of the reagent would have made the determinations interminable, so this arbitrary ending of the reaction was chosen. For comparative purposes and for the purposes of this investigation the data so secured were quite sufficient. The time required for an absorption was about one and one-half hours. Between each determination the gas buret was detached from the pipet, the residual liquor run out through K, and the pipet cleaned and dried.

TABLE II.  
Volume of Oxygen Absorbed by Sodium Pyrogallate.

	Pyrogallie acid (g.).	Water (g.).	Stock soln. NaOH (cc.) <sub>5</sub>	Proportions by weight of absorbing constituents.			Oxygen absorbed by 1.5 cc. reagent (cc.).
				NaOH.	Pyrogallie acid.	Water.	
1.....	1	+1	10.0	7.36	1.00	8.62	46.6
2.....	1.5	+1	10.0	7.36	1.50	8.62	69.0
3.....	2.0	+1	10.0	7.36	2.00	8.62	81.5
4.....	2.5	+1	10.0	7.36	2.50	8.62	104.0
5.....	3.0	+1	10.0	7.36	3.00	8.62	113.0
6.....	5.0	+3	10.0	7.36	5.00	10.62	132.0
7.....	7.0	+3	10.0	7.36	7.00	10.62	170.7
8.....	10.0	+3	10.0	7.36	10.00	10.62	232.2
9.....	10.0	+4	10.0	7.36	10.00	11.62	222.6
10.....	12.0	+4	10.0	7.36	12.00	11.62	265.2

The densities of reagents No. 1 and No. 9 were determined at 20°/4 in an Ostwald-Sprengel pycnometer. Knowing the composition by weight of these reagents the density formed a ready and accurate means of determining the concentration of the constituents in the 1.5 cc. volume used.

**Comparison with Potassium Pyrogallate.**—Comparative determinations were made in the same apparatus using potassium pyrogallate instead of the sodium salt. 10 cc. of a solution of potassium hydroxide, made by dissolving 73.4 g. of stick alkali in 73.4 cc. of water were added to 10 g. of pyrogallie acid. 1.5 cc. of this solution absorbed 223 cc. of oxygen before the rate of absorption dropped to 1 cc. in 10 minutes. This

is practically the same volume as that for sodium pyrogallate of the same concentration. But absorption of the oxygen from 50 cc. of air under conditions identical with those for sodium pyrogallate required from 6 to 10 minutes instead of from 2 to 4 minutes as with the sodium salt.

3.5 cc. of the reagent, as prepared above, were diluted with 1 cc. of water. 1.5 cc. of this solution absorbed 197 cc. of oxygen before the rate of absorption had dropped to 1 cc. in 10 minutes. Complete absorption in four minutes was also obtained, but this continued only until 60 cc. of oxygen had been absorbed.

The dropping off in the rate of absorption for solutions containing a high concentration of pyrogallol limits the use of potassium pyrogallate to solutions of relatively low specific absorption. Anderson found that the specific absorption with 15 g. of pyrogallol in 100 cc. of solution was almost equal to that with 20 g. per 100 cc. But with sodium pyrogallate there is no such dropping off in specific absorption, and reagents containing 50 g. of pyrogallol per 100 cc. of solution are perfectly practicable.

It was also considered desirable to determine in our apparatus the absorption of oxygen by the potassium pyrogallate reagent recommended by Anderson as being the best solution for use in the Hempel double pipet. 1.5 cc. of this reagent absorbed about 30 cc. of oxygen from the air before the absorption was incomplete in 4 minutes and about 70 cc. of 95% oxygen before the rate of absorption dropped to 1 cc. in ten minutes. In comparison, the sodium pyrogallate of reagent No. 9 absorbed 154 cc. of oxygen from the air before absorption was incomplete in four minutes, and 222.4 cc. before the rate fell below 1 cc. in ten minutes. The reagent proposed by us has, therefore, five times the specific absorption of that recommended by Anderson as being the best for potassium pyrogallate.

**Volume of Oxygen Absorbed before Rate of Absorption Dropped to Four-minute Limit.**—For practical purposes the value of a reagent for the absorption of a gas ceases when the rate of absorption has decreased below a certain value. In this work complete absorption of the oxygen from 50.0 cc. of air when absorbed in the simple pipet, Fig. 2, was chosen as the limit.

1.5 cubic centimeter portions of solution No. 9 were treated with successive 50.0 cc. volumes of air at 20°, the residual gas being run off after each absorption. This was continued until absorption failed to be complete in four minutes with two transfers of the gas back to the buret. The average of three closely agreeing results gave 180 cc. of oxygen absorbed. Three similar absorptions carried out by first absorbing 125 to 130 cc. of oxygen from the 95% sample and then completing the determinations with 50.0 cc. volumes of air gave 154, 155 and 154 cc. of oxygen absorbed before the rate dropped below the four-minute limit.

Similar determinations on 1.5 cc. portions of solution No. 1 gave an absorption of about 20 cc. before the four-minute limit was reached.

The difference in the specific absorptions as found above for the same solution depending on the percentage of oxygen used, is, according to Hempel and Anderson,<sup>1</sup> the result of the deleterious effect of high temperature. With 95% oxygen the rise of temperature in the reagent was very marked indeed.

**Rate of Absorption.**—Two series of measurements of the rate of absorption of oxygen by the proposed reagent were made. The first consisted in observing the volume of oxygen absorbed by 1.5 cc. of the reagent in four minutes from successive 50.0 cc. portions of air together with the time required for complete absorption. The results for solution No. 9 are included here but they are typical of all. Only the last six observations are given, since all before these were identical with the 1st and 2nd.

50.0 cc. portion of air.	Vol. ab- sorbed in 4 minutes. Cc.	Time for complete absorption of oxygen. Minutes.	50.0 cc. portion of air.	Vol. ab- sorbed in 4 minutes. Cc.	Time for complete absorption of oxygen. Minutes.
1st.....	10.4	4	4th.....	9.2	11
2nd.....	10.4	4	5th.....	7.6	18
3rd.....	10.0	6	6th.....	4.0	50

The time necessary for complete absorption increased very rapidly. This is of special significance to the gas analyst. As soon as the rate of absorption of alkaline pyrogallate begins to drop off the reagent should be replaced by fresh solution, thus obviating the danger from incomplete absorption in a reasonable interval of time.

The second series of observations was made on the falling off in the rate of absorption when complete exhaustion of the reagent was being approached. The results for three solutions are plotted in Fig. 3. The ordinates represent the volume of oxygen absorbed by 1.5 cc. of the reagent when a considerable excess of 95% gas was present, while the abscissae indicate the time intervals in minutes corresponding to the volume reading. These observations were taken with the special apparatus already described and were accompanied by frequent passing back and forth of the gas between the pipet and the buret. Curve A is for solution No. 8 and requires to have 90.0 cc. added to it, since observations were not taken until the curve began to leave the vertical. Similarly Curve B, representing solution No. 6, must have 20 cc. added to it, while Curve C is that for solution No. 2 and represents the total volume of oxygen absorbed. The curves end when the rate of absorption had dropped to that of 1 cc. in ten minutes. The vertical portion of the curves, representing 210 cc. for solution No. 7, 120 cc. for No. 6 and 50 cc. for No. 2, indicates the volume of oxygen that might be absorbed by 1.5 cc. of

<sup>1</sup> Anderson, *Loc. cit.*

the respective reagents before exhaustion made further use of the reagent in gas analysis doubtful. The three curves are practically parallel and have the general direction of curves representing a reaction following the law of mass action.

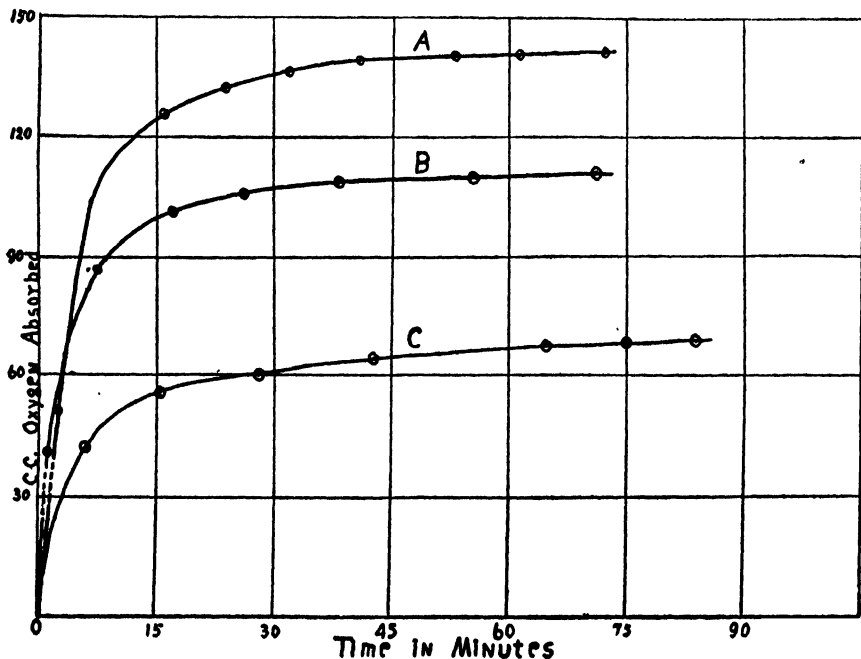


Fig. 3.

**Temperature Coefficient.**—A series of determinations was carried out to establish the relationship of temperature to the rate of absorption. The time required by solution No. 9 to completely absorb the oxygen from equal volumes of air at different temperatures was taken as the basis for comparison. The absorption pipet was surrounded by a bath kept at the desired temperature and 50.0 cc. portions of air were run in from the gas buret, the time for complete absorption being noted. The gas was run back and forth twice in each case, excepting at the higher temperatures where absorption was complete without doing so. At temperatures above 40.0° absorption was so rapid that the time measurements could not be made with any degree of accuracy. The series, however, follows in general the law of Ostwald that the speed of a reaction doubles for each 10° rise in temperature. It also disposes of the contention<sup>1</sup> that alkaline pyrogallate is very much less active at a temperature of 7° than at 15°.

<sup>1</sup> Hempel, "Gas Analysis," 1916, p. 149.

TABLE III.—TEMPERATURE COEFFICIENT.

Temperature centigrade.....	0.0°	10.0°	15.0°	20.0°	25.0°	30.0°	40.0°	45.0°
Time for complete absorption, minutes.....	8-10	8	6	4-5	3	2	1	1

**Relation of Oxygen Absorbed to Amount of Pyrogallol.**—Table II contains the results of determinations made with ten different proportions of acid, alkali and water, ranging in concentration from a reagent containing but 10 g. of pyrogallol in 110 cc. of solution to a reagent from which sodium pyrogallate separated on cooling. It will be observed that the absolute alkali content was not varied throughout the series, that the water content was changed twice while the pyrogallic acid content was increased for each determination. At high concentration it was found necessary to increase the water content in order to prevent the crystallization of sodium pyrogallate and the consequent clogging of the apparatus. The composition of solutions No. 1 and No. 9 in respect to pyrogallol alkali and water may easily be calculated from the weight of these constituents used and the determined densities. The density of any of the intermediate solutions of Table II lies between that of 1.490 for No. 1 and 1.405 for No. 9. A slight increase in volume occurs as the pyrogallic acid content of a water solution increases so that direct comparison between the 1.5 cc. portions of the reagents used and the volumes of oxygen absorbed does not give the exact relation existing between pyrogallic acid and oxygen absorbed. But the results given in Table II indicate clearly that the absorption capacity is roughly directly proportional to the pyrogallic acid content.

Another cause of irregularity in this proportion was occasioned by the variable conditions under which the absorption of oxygen took place. A rapid rise in temperature always occurred and this rise was more marked for the solutions containing the higher proportions of pyrogallol. Moreover, since the gas used contained only 95% oxygen the residual gas contained varying proportions of oxygen for each determination. The residual gas containing the least proportion of oxygen would reach the chosen limit of absorption first. Replacing the residual gas with 60 cc. of 95% oxygen gave an increased absorption of 10 cc. to reagent No. 9 before the limit was reached.

Solution No. 10 was very viscous and on standing sodium pyrogallate crystallized out. For this reason further experimentation was carried out with the less concentrated solution No. 9.

The volume of oxygen absorbed by each gram molecule of  $C_6H_6O_3$  present in reagents No. 1 and No. 9 was calculated from the known weight of alkali, acid and water taken and the determined densities. Calculations based on the results given in Table II gave an absorption of 63.1 g. of oxygen for each gram molecule of  $C_6H_6O_3$  present in reagent No. 9.

and 59.1 g. for reagent No. 1. The result for the former was based on the complete exhaustion of the reagent while for the latter only to when the rate of absorption had become 1 cc. in ten minutes. Berthelot<sup>1</sup> found that for complete absorption with the sodium pyrogallate and potassium pyrogallate reagents he used, 48.5 g. of oxygen were absorbed per gram molecule of  $C_6H_6O_3$ , or three atoms of oxygen per molecule of  $C_6H_6O_3$ . Our results are from 30% to 40% higher than this and apparently do not follow so simple a proportion. Calculating the intermediate reagents of Table II on the basis of a density of 1.49 or 1.41 (between which limits the densities of the solutions must lie) gave results in every case much higher than those of Berthelot. With ammonium pyrogallate Berthelot obtained 66.4 g. of oxygen absorbed per gram molecule of  $C_6H_6O_3$ . Considering the variety of the oxidation products formed it seems unlikely that a simple relationship would exist between the oxygen absorbed and the  $C_6H_6O_3$  present, but that this relation would be a function of several variables such as temperature, viscosity, nature of absorbing vessel, relative concentration of oxygen, acid and alkali, etc. This view is consonant with the experimental evidence,<sup>2</sup> for by changing the conditions of oxidation for the same reagent carbon monoxide may or may not be formed, indicating clearly a marked change in the nature of the oxidation products. Moreover, it has been frequently observed that the temperature at which absorption takes place and the percentage of oxygen in the gas reacting affects the amount of oxygen absorbed.

De Forcrand<sup>3</sup> was not able to prepare pure mono and disodium pyrogallate from the reaction between sodium hydroxide and pyrogallic acid in aqueous solution. He always obtained a product containing a considerable proportion of resinous matter, and this when the reaction was carried out in an atmosphere of hydrogen. Trisodium pyrogallate on the other hand separated pure. One might expect, therefore, that with an excess of alkali present the absorption of oxygen would be more uniform, but Berthelot found that so long as he did not reduce the molecular proportions of alkali and pyrogallol below that of 1 : 1 the amount of oxygen absorbed remained the same as when the proportion was 3 : 1.

**The Formation of Carbon Monoxide.**—Throughout the course of this research numerous determinations were made for the detection of carbon monoxide in the residual gas after complete exhaustion of the reagents. The excess oxygen from the residual gas was absorbed in an Orsat pipet containing sodium pyrogallate reagent No. 5, Table II. After the complete absorption of the oxygen as indicated by no further change in volume on remaining in contact with the reagent for some time the gas was passed

<sup>1</sup> Berthelot, *Loc. cit.*

<sup>2</sup> Clowes, *Loc. cit.* This paper, p. 1699.

<sup>3</sup> De Forcrand, *Compt. rend.*, 115, 46, 48 (1892).

into another Orsat pipet containing freshly prepared ammoniacal cuprous chloride. Two such pipets were prepared, but as carbon monoxide was only found in one instance the second pipet was quite superfluous. To remove ammonia the gas was finally passed into a pipet containing a dilute solution of sulfuric acid. In order to be sure that the cuprous chloride pipet was functioning properly, air containing carbon monoxide was passed through the system of pipets in the same order as was the residual gas. A decrease in volume corresponding to the known amount of carbon monoxide in the gaseous mixture occurred in the cuprous chloride pipets. This check was run twice during the course of the analyses and once at the close.

No measurable quantity of carbon monoxide was detected in any of the reagents included in Table II. Special attention was given the proposed reagent No. 9, exhaustion being brought about under the varying conditions likely to occur in the application of this reagent for use in gas analysis. Speedy exhaustion with 95% oxygen and consequent high temperature of reaction, slow successive additions of oxygen without rise of temperature and exhaustion by successive volumes of air, all alike gave no appreciable absorption in freshly prepared cuprous chloride solution. One sample of gas was kept in contact with the reagent for a week after exhaustion was about complete, but no carbon monoxide was evolved. The potassium pyrogallate reagent, as recommended by Anderson, also failed to evolve any appreciable quantity of this gas. Experiments were next carried out with the sodium hydroxide reagent of Lewes. No generation of carbon monoxide was obtained when successive volumes of air were employed, but when 95% oxygen was used over 3.0 cc. of carbon monoxide was formed. This is in agreement with Clowes, who found that no carbon monoxide was formed when the gas contained less than 28% oxygen, but above that percentage the quantity became appreciable and increased as the alkali content was diminished. Evidently the alkali content used in the series of Table II was sufficient to prevent the formation of this objectionable gas in appreciable amounts. The non-formation of carbon monoxide was indirectly corroborated for the above reagents by the complete absorption of the oxygen from the air. Many determinations on 50.0 cc. volumes of air were made when the rate of absorption was under investigation. If carbon monoxide had been evolved in appreciable amounts it would have been indicated as incomplete absorption. Such did not occur in any one of the reagents listed in Table II. The volume of oxygen absorbed always agreed with that corresponding to the percentage composition in the atmosphere.

Concerning the conditions favoring the formation of carbon monoxide it may be pointed out that solution No. 9 contains only 2.3 molecules



of sodium hydroxide per molecule of pyrogallol while 3 molecules would be necessary for complete neutralization. The absence of carbon monoxide does not, therefore, appear to be dependent upon having an excess of alkali present as Clowes<sup>1</sup> contends.

**Rate of Absorption in Various Pipets.**—It was deemed desirable to try the proposed reagent in several different pipets. The table below gives briefly the results of these determinations.

TABLE IV.

Time of complete absorption of oxygen from 100.0 cc. air.

Reagent.	Hempel pipet.	Richards pipet.	Orsat pipet.	New pipet.
No. 9.....	10-15 min.	10-15 min.	4-6 min.	4-6 min.
No. 5.....	.....	.....	4-6 min.	4-6 min.

Complete absorption was obtained with from three to four transfers for the Orsat and the New pipet while with the Richards and the Hempel pipets double as many transfers combined with continual shaking failed to obtain complete absorption in less than ten minutes. Rhodes<sup>2</sup> found that nine minutes accompanied by nine transfers back and forth were necessary to obtain complete absorption of the oxygen from 100.0 cc. sample of air using the Orsat pipet and potassium pyrogallate.

It is hard to understand why the Hempel pipet should be longer used for any but very special work. It is difficult to fill with any reagent and especially so if the reagent is somewhat viscous. The long bent capillary is a source of weakness in structure and of irregularity in use. The enormous friction of the liquid in the capillary requires, even with comparatively fluid reagents, a considerable excess of pressure to overcome and prohibits entirely the use of many concentrated reagents because of their viscosity. Moreover the pipet requires a special and expensive stand while shaking has to be resorted to in order to obtain efficient absorption. Should the pipet be broken anywhere only an experienced glass blower can repair it.

The Richards pipet is much simpler but is objectionable because of the necessity for shaking. Moreover having the bulbs above the stoppers with a comparatively long stem extending down to the bottom of the bottles gives an objectionable hydrostatic pressure when the apparatus is in use. The new pipet combines the good points of the Richards model with those of the Orsat type.

**Choice of Reagents for Gas Analysis.**—Table V gives the relative absorption capacity of 150 cc. of solutions No. 1 and No. 9 and the best KOH reagent as proposed by Anderson.

<sup>1</sup> Clowes, *J. Soc. Chem. Ind.*, 15, 170 (1896).

<sup>2</sup> Dennis, "Gas Analysis," p. 82.

TABLE V.

Volume of oxygen absorbed by 150 cc. of reagent before reaching four-minute limit.

Reagent.....	No. 1	No. 9	Best KOH reagent
Volume of oxygen absorbed, liters.....	2.2	15.3	3.0

Such a reagent as No. 9 is, therefore, five times as efficient an absorbing agent for oxygen as the best potassium pyrogallate solution.

Reagent No. 9 is somewhat viscous and in pipets provided with capillaries less than 1.5 mm. in internal bore, difficulty may be found in driving over the last portions of gas. With larger capillaries this reagent causes no difficulty whatsoever. Should a particular pipet have a small-bore capillary it would be advisable to use a more fluid reagent, such as No. 3 or No. 5.

Should difficulty in observing the position of the meniscus in the capillary be encountered because of the highly colored and viscous nature of the oxidation products, the running over of a very little water from the gas buret readily clears the tube for the final reading.

Such a reagent as No. 9 should replace in technical gas analysis the use of the more expensive and less efficient potassium solution. The saving of time and trouble in using a reagent lasting five times as long should alone decide in its favor. For use in a laboratory course in gas analysis, where only a comparatively small volume of oxygen is to be absorbed, reagent No. 3 would be found eminently satisfactory. Reagents No. 3 and No. 9 have been used in the laboratory classes of Ohio State and have proved quite satisfactory in every respect. No deterioration in the reagents was observed over a period of three months.

**The Use of Ammonium and Barium Pyrogallate.**—A reagent prepared by dissolving 10.0 g. of pyrogalllic acid in 10.0 cc. of 29% ammonium hydroxide precipitated on cooling a white crystalline substance soluble on heating but again separating on cooling. On adding 10.0 cc. more of the ammonium hydroxide the precipitate failed to dissolve. Evidently the trihydroxy benzene compound with ammonia is much less soluble than those of sodium hydroxide and potassium hydroxide. A second solution prepared by dissolving 10.0 g. of pyrogallol in 10.0 cc. of water and adding 160 cc. of 29% ammonium hydroxide gave complete absorption of the oxygen from 50.0 cc. of air in five minutes. Apparently, if occasion required, ammonium pyrogallate might be used for absorbing oxygen.

The insoluble barium compound of trihydroxy benzene made it impracticable for use in any but a very dilute solution. Moreover, the oxygen compound formed appeared to be insoluble and tended to clog the capillary connecting tube of the absorption apparatus while at the same time the rate of absorption was very low.

### Summary.

- (1) A new double pipet for liquid reagents in gas analysis is described.
- (2) The use of sodium pyrogallate as a reagent for the determination of oxygen in gases is proposed. Complete absorption in four minutes was secured from a number of solutions containing pyrogallol, sodium hydroxide and water in varying proportions. No carbon monoxide was detected in using the proposed reagent under varying conditions and the specific absorption of the best practicable solution was found to be five times that of the corresponding best solution for potassium pyrogallate.
- (3) The total volume of oxygen absorbed was found to be in excess of the proportion of 3 atoms of oxygen for each molecule of pyrogallol.
- (4) Ammonium and barium pyrogallate were found to be impracticable for general use in gas analysis.

COLUMBUS, OHIO.

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[CONTRIBUTION FROM THE KENTUCKY AGRICULTURAL EXPERIMENT STATION.]

## THE ESTIMATION OF THIOSULFATE SULFUR IN LIME-SULFUR SOLUTIONS BY IODINE TITRATION.

BY PHILIP L. BLUMENTHAL AND S. D. AVERITT.

Received May 10, 1916.

The question of the accuracy of the so-called "Iodine Methods" for the estimation of thiosulfates and polysulfids in commercial lime-sulfur solutions has vexed agricultural chemists for some years past. Recently one of us<sup>1</sup> published a paper in which he proved that the substance titrated with iodine after removing polysulfids, actually was thiosulfate, by means of a process in which tetrathionate was reconverted to thiosulfate and estimated.

Roark<sup>2</sup> stated that in the iodine titration there is reason to believe that iodine may cause an increased formation of sulfate, thus introducing an error.

We have undertaken to test the accuracy of the iodine method for thiosulfate in another fashion, namely, by converting the tetrathionate formed to sulfate and comparing this value with the titration figure.

### Experimental.

The following experiments were conducted with two objects in mind: to ascertain whether the oxidation of thiosulfate or tetrathionate to sulfate occurs sufficiently rapidly and in such quantity, particularly under poor working conditions, as to cause serious analytical errors; and to learn as much as possible about the chemistry of the lime-sulfur titration after the removal of polysulfid sulfur.

<sup>1</sup> S. D. Averitt, *J. Ind. Eng. Chem.*, **8**, 623 (1916).

<sup>2</sup> *J. Assoc. Off. Agr. Chem.*, **1**, 65.

Three portions of 0.05 *N* (factor 0.9948 0.05 *N*) thiosulfate were titrated exactly with approximately 0.1 *N* (factor 0.995 0.1 *N*) iodine solution to form tetrathionate, and a definite excess of iodine was added to each. The solutions were well stoppered and allowed to stand in the dark for two weeks. BaCl<sub>2</sub> was then added and the BaSO<sub>4</sub> weighed. Where the ratio of iodine to thiosulfate in two experiments was approximately 2 : 1, about 18% of the sulfur present was found as sulfate; with the ratio 3<sup>1</sup>/<sub>2</sub> to 1 in another experiment about 36% of the sulfur was found as sulfate. In each case, the blank for sulfate originally present in the thiosulfate was deducted. Evidently a considerable oxidation of *tetrathionate* occurred under the conditions of the experiment.

It is, therefore, conceivable that in a titration, if the iodine were to be run into a thiosulfate solution rapidly, without constant shaking, the formation of regional excesses of iodine might cause a slight oxidation of some of the tetrathionate first formed, to sulfate. In most cases this error would be small, since in a titration there is usually only a very short time in which iodine is in excess, and the action upon tetrathionate is by no means rapid.

To get an idea of the possible extent of this action, under working conditions, a series of experiments was conducted as follows:

Ten portions of 20 cc. each of a thiosulfate solution (0.1 *N*) were treated as follows: 1 and 2 had 2 cc. 10% BaCl<sub>2</sub> added and were then allowed to stand overnight, to permit the sulfates present to separate out. This served as a control on the sulfate content of the thiosulfate solution. 3 and 4 were carefully titrated with iodine solution, with constant shaking, so as to avoid regional excesses of iodine, and afterward the same amount of BaCl<sub>2</sub> was added. 5 and 6 were rapidly titrated, permitting regional excesses of iodine to form, shaking only toward the end of the titration so as to simulate careless work; after completion, BaCl<sub>2</sub> was added. 7 and 8 were similar to 3 and 4, except that BaCl<sub>2</sub> was added before titrating to remove SO<sub>4</sub> ions as rapidly as formed. 9 and 10 also had BaCl<sub>2</sub> added first and were otherwise identical with Nos. 5 and 6. To all except Nos. 1 and 2 a little 0.1 *N* HCl was added after the titration to prevent BaS<sub>4</sub>O<sub>6</sub> formed from decomposing, experience having shown that HCl stabilizes the barium salt. The average weight of BaSO<sub>4</sub> obtained in each pair was as follows: 0.55, 0.90, 0.95, 1.25 and 1.25 mg., respectively. The quantity of sulfate produced in the last four sets (3-10 inclusive) by the action of iodine upon tetrathionate was, therefore, 0.35, 0.4, 0.7 and 0.7 mg., respectively. A slight difference in the iodine titration values could be noticed. The averages of the titrations were 19.82 cc., 19.85 cc., 19.84 cc. and 19.86 cc., respectively, the maximum difference being 0.04 cc. in Nos. 9 and 10 as compared to Nos. 3 and 4. The differ-

ence in weight of  $\text{BaSO}_4$  between the averages of the same two sets is 0.35 mg. It would require 0.048 cc. of 0.1 *N* I to produce this amount of  $\text{BaSO}_4$  according to the equation  $\text{Na}_2\text{S}_4\text{O}_6 + 7\text{I}_2 + 10\text{H}_2\text{O} = 2\text{NaHSO}_4 + 2\text{H}_2\text{SO}_4 + 14\text{HI}$ , a good agreement considering the difficulty of estimating such small quantities. However, even if iodine does oxidize thiosulfate or tetrathionate all the way to sulfate, the quantity so produced in a lime-sulfur analysis would be almost negligible (less than 0.01% S), since the quantity of thiosulfate here employed is four to eight times as great as one encounters in actual analysis, according to the official procedure. It seems probable that in every titration a small quantity of iodine is used to produce sulfates by direct oxidation; we know of no method to prove this directly, since the error of weighing thiosulfate as  $\text{BaSO}_4$  is fully as great as the titration error, and there is no other method<sup>1</sup> known to us of standardizing a thiosulfate solution except by iodine titration of one kind or another.

In order to throw further light upon this sulfate-forming reaction and also upon the iodine titration methods as applied to lime-sulfur solutions, some experiments were carried out upon three lime-sulfur solutions which had already been analyzed by one of us (Averitt) during the progress of the work. Nos. 1 and 3 were commercial concentrates, No. 2 was made in the laboratory from pure chemicals and had a high thiosulfate content.

Three aliquots of Sample No. 1 were titrated with HCl to incipient acidity to methyl orange, the hydrogen sulfid was boiled out and  $\text{BaCl}_2$  added. The precipitated sulfur (and barium sulfate, if present) was filtered on fine-mat Gooch crucibles, dried, ignited and weighed. No barium sulfate was found, indicating absence of sulfate in the sample and reagents and that no sulfate was formed during the removal of  $\text{H}_2\text{S}$ . Similar results were obtained upon samples Nos. 2 and 3.

A second set of three aliquots each of Nos. 1 and 2 was treated as before with HCl and boiled and, after  $\text{BaCl}_2$  and starch had been added, the solution (containing precipitated sulfur) was titrated with approximately 0.1 *N* iodine solution. The iodine consumed represents thiosulfates and sulfites, if the latter are present—a disputed point. After standing overnight, a small amount of  $\text{BaSO}_4$  was found which, on each series of aliquots, averaged 0.7 mg. and 1.2 mg. of  $\text{BaSO}_4$ , respectively. This sulfate must have resulted either from the oxidation of sulfite or from the interaction of thiosulfate or tetrathionate with iodine.

Ashless paper filters were substituted for the Gooch crucibles after this, as it was found difficult to retain very small quantities of sulfate on asbestos.

<sup>1</sup> We have since heard of another method of standardization and hope to test it at a later period.

Three portions of 0.05 *N* (factor 0.9948 0.05 *N*) thiosulfate were titrated exactly with approximately 0.1 *N* (factor 0.995 0.1 *N*) iodine solution to form tetrathionate, and a definite excess of iodine was added to each. The solutions were well stoppered and allowed to stand in the dark for two weeks. BaCl<sub>2</sub> was then added and the BaSO<sub>4</sub> weighed. Where the ratio of iodine to thiosulfate in two experiments was approximately 2 : 1, about 18% of the sulfur present was found as sulfate; with the ratio 3<sup>1</sup>/<sub>3</sub> to 1 in another experiment about 36% of the sulfur was found as sulfate. In each case, the blank for sulfate originally present in the thiosulfate was deducted. Evidently a considerable oxidation of *tetrathionate* occurred under the conditions of the experiment.

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Ashless paper filters were substituted for the Gooch crucibles after this, as it was found difficult to retain very small quantities of sulfate on asbestos.

<sup>1</sup> We have since heard of another method of standardization and hope to test it at a later period.

Next, three portions, each containing 1 gram of concentrate (No. 3) were treated as follows: One portion, after being titrated with HCl, having BaCl<sub>2</sub> added and H<sub>2</sub>S boiled out, was titrated with iodine and allowed to stand several hours. The BaSO<sub>4</sub> weighed 1.0 mg. The filtrate was then oxidized with bromine and the barium sulfate weighed. Calculated from this figure, the thiosulfate sulfur was 0.51%, which was exactly the same as the iodine titration value.

The other two portions were titrated with HCl as before and the H<sub>2</sub>S was boiled out. After filtering out the precipitated sulfur, barium chlorid was added and the solution allowed to stand overnight. No precipitate was found, which proved the absence of sulfate in the original sample and also that none was formed during the removal of H<sub>2</sub>S by boiling from a barely acid solution. The samples were then titrated with iodine and allowed to stand overnight before filtering. The barium sulfate found weighed 1.2 and 1.1 mg., respectively. This sulfate came either from the presence of a small amount of sulfite or from the action of iodine on the tetrathionate or thiosulfate. The barium sulfate weighed from the oxidation of tetrathionate by bromine showed 0.51 and 0.54% sulfur as compared to 0.52 and 0.54% by the iodine titration.

### Conclusions.

The following points are considered as being established:

1. An excess of iodine does react with tetrathionate in neutral or faintly acid solutions, upon standing.
2. In every iodine titration on a lime-sulfur solution a small quantity of sulfate is formed; in some lime-sulfur solutions this is the only sulfate found.
3. The quantity of iodine used to form sulfate in an ordinary titration does not cause an appreciable error in the determination of thiosulfate.
4. The iodine values obtained after decomposing polysulfids by HCl titration actually represent thiosulfate, since the barium sulfate obtained from such solutions after oxidation agrees very closely with the titration values. The presence of sulfites, which would also be titrated at this point, would tend to cause high results for thiosulfate as calculated from the iodine value. If anything, the gravimetric results for thiosulfate are a trifle higher than the titration values, which points to an absence of sulfites, although this in itself is not absolute proof of the fact.

The authors are now investigating the velocity of the reaction between iodine and sodium tetrathionate in neutral and acid solution, and will present these results shortly. They desire to extend their sincere thanks to Dr. A. M. Peter, of this laboratory, for kind and helpful suggestions, during the progress of this work.



[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PURDUE UNIVERSITY.]

## DETECTION OF NICKEL IN COBALT SALTS.

BY A. R. MIDDLETON AND H. L. MILLER.

Received June 27, 1916.

The use of dimethylglyoxime as a reagent for the detection and determination of nickel, discovered by Tschugaev<sup>1</sup> in 1905 and developed by Brunk,<sup>2</sup> has become quite general. In addition to its simplicity of manipulation and freedom from interference by other metallic ions this reagent is unusually delicate. The brilliant scarlet color and extreme insolubility of nickel glyoximine<sup>3</sup> permits detection of one part of nickel in at least 350,000 parts of water and a modified method of using the reagent will be described in this paper by which we have been able to detect one part of nickel in more than 4,000,000 parts of water.

For the detection of traces of nickel in cobalt salts this reagent has not proved entirely satisfactory.<sup>4</sup> Cobalt combines with dimethylglyoxime to form an extremely soluble compound of brown color. Either because the nickel salt is soluble in this compound or, more probably, because the cobalt appropriates most of the reagent, no nickel is precipitated by ordinary amounts of reagent from cobalt salt solutions even though a considerable amount is present. The object of this investigation was to devise a method by which the cobalt ion should be suppressed, thus permitting the reagent to react with nickel only and avoiding the necessity for large amounts of reagent. Treadwell,<sup>5</sup> following a suggestion of Tschugaev, accomplishes this result by transforming the cobalt salt into a cobaltic ammine by concentrated ammonia and hydrogen peroxide before adding dimethylglyoxime. We shall show that this method is unsatisfactory and fails when much cobalt is present.

The most striking differences in the chemical behavior of nickel and cobalt are (1) the greater susceptibility of the latter to oxidation to the trivalent condition, and (2) the greater stability of its complex ions, both positive and negative. Of the various complex ions formed by cobalt the most stable are the complex cyanides, that of trivalent cobalt being decidedly more stable than that of bivalent cobalt. Nickel forms complex cyanides of a different type, resembling those of bivalent copper, whereas the cobalt cyanides are analogous to the iron cyanides. In the classic method of Liebig<sup>6</sup> for detecting nickel in cobalt salts, the inferior stability of the nickelocyanide ion together with the ready oxidizability of cobaltocyanide to cobalticyanide has long been used to effect a separation. For

<sup>1</sup> *Ber.*, 38, 2520 (1905).

<sup>2</sup> *Z. angew. Chem.*, 20, 3444 (1907).

<sup>3</sup> The nomenclature of Tschugaev, *Z. anorg. Chem.*, 46, 147 (1905).

<sup>4</sup> Cf. E. F. Smith, *Trans. Am. Electrochem. Soc.*, 27, 31 (1915).

<sup>5</sup> *Analyt. Chem.*, 1, 151, 7th ed.

<sup>6</sup> *Ann.*, 65, 244 (1848); 87, 128 (1853).

a solution containing cobalticyanide, nickelocyanide and cyanide ions the following equilibria are involved:



The values of the instability constants are not accurately known, but it is certain that that of the cobalticyanide ion is extremely small and that of the nickelocyanide ion much larger. Any reduction of the concentration of the cyanide ion in the solution must result in decomposition of the nickelocyanide ion and considerable increase of nickel ion concentration while the much more stable cobalticyanide ion is less affected. In Liebig's method as modified by Gauhe<sup>1</sup> the cyanide ion is removed by oxidation with alkaline hypochlorite or hypobromite, the nickelous ion being simultaneously oxidized and precipitated as nickelic hydroxide. This method is not altogether satisfactory because cobaltic hydroxide is usually precipitated also and the appearance of a brown precipitate is by no means certain proof of the presence of nickel.

Since nickel glyoximine is decomposed by the cyanide ion, our problem was to remove the cyanide ion so gradually that the cobalticyanide ion should remain practically unaffected. For this purpose we have made use of the great stability of complex silver cyanide ions, together with the small solubility of silver argenticyanide,  $\text{Ag}[\text{Ag}(\text{CN})_2]$ , 0.0004 g. per liter at 20°.<sup>2</sup> For argenticyanide ion,  $[\text{Ag}'] \times [\text{CN}']^2 = 10^{-21} \times [\text{Ag}(\text{CN})_2']$ .<sup>3</sup> The comparative insolubility of silver cobalticyanide, accurate data for which are lacking, should also tend to prevent decomposition of the cobalticyanide ion. If to a solution containing alkali salts of nickelocyanide, cobalticyanide and a small excess only of cyanide, dimethylglyoxime be added and then dilute silver nitrate solution gradually, precipitation of silver argenticyanide removes the cyanide ion and promotes decomposition of the nickelocyanide ion, increasing the concentration of the nickelous ion, while the cobalticyanide ion is precipitated as  $\text{Ag}_3\text{Co}(\text{CN})_6$ , or, if not precipitated, is but slightly decomposed. Comparatively little dimethylglyoxime should then be sufficient to precipitate the small amount of nickel present, in part at least. The experiments recorded below show that this modification yields very satisfactory results.

### Experimental.

**Solutions and Reagents.**—Nickel sulfate solution from Kahlbaum's "Kobalt-frei" salt was standardized by electrolysis (0.05008 *N* and by precipitation and weighing as glyoximine 0.04968 *M*). Cobalt, if present, was in very small amount; we were unable to detect it with absolute certainty. Iron was found present and the discrepancy in the electrolytic

<sup>1</sup> *Z. analyt. Chem.*, **5**, 75 (1866).

<sup>2</sup> Bredig, *Z. physik. Chem.*, **46**, 602 (1903).

<sup>3</sup> Bodländer, *Z. anorg. Chem.*, **39**, 227 (1904).

and precipitation values is probably due almost entirely to its presence. Its removal appeared unnecessary for our purpose. The more dilute solutions used in the work were prepared from this solution by accurate dilution.

Cobalt sulfate solution, approximately 0.1 *M*, was prepared by working up residues from cobalt ammine salts. Nickel was removed by dimethylglyoxime according to the method we have developed and the solution as used gave no test for nickel. By electrolysis this solution was found to be 0.0921 *M*.

The other reagents used were: potassium cyanide, 10% solution; dimethylglyoxime, 1% solution in alcohol; and silver nitrate 1% solution.

**Sensitiveness of Dimethylglyoxime as Reagent for Nickel in Absence and in Presence of Silver Cyanide.**—Two 10 cc. portions of each of the  $\text{NiSO}_4$  solutions of the concentrations stated in Table I were taken. One was warmed to about 80°, 1 cc. of the dimethylglyoxime reagent added and a drop or two of dilute ammonia. The other portion was converted into the complex cyanide by adding two or three drops of KCN. At these small concentrations no precipitate of nickel cyanide was formed. The solution was warmed to 80°, 1 cc. of dimethylglyoxime reagent added, and then  $\text{AgNO}_3$  solution dropwise until a permanent white or pink precipitate formed. The more concentrated solutions thus treated gave at once pink precipitates; the more dilute ones white precipitates which turned pink on standing. In those solutions which required more than one hour to form a precipitate the exact time required for the pink color to appear was not recorded. In these cases the samples were observed after standing 24 hours. In the extreme dilutions of the simple ion the precipitate was frequently a single red crystal, very minute and difficult to see.

TABLE I.

Molar conc.	$\text{NiSO}_4$ .	$\text{K}_2\text{Ni}(\text{CN})_4$ .	Mg. Ni per cc.	Dilution.
0.0005	Immediate	Immediate	0.02934	$1:0.034 \times 10^6$
0.00005	1 hr.	3 min.	0.002934	$1:0.34 \times 10^6$
0.00001	24 hr.	5 min.	0.000587	$1:1.7 \times 10^6$
0.000009	24 hr.	10 min.	0.000528	$1:1.9 \times 10^6$
0.000008	24 hr.	20 min.	0.000470	$1:2.13 \times 10^6$
0.000007	24 hr.	30 min.	0.000411	$1:2.43 \times 10^6$
0.000006	24 hr.	1 hr.	0.000352	$1:2.84 \times 10^6$
0.000005	24 hr.	24 hr.	0.000293	$1:3.4 \times 10^6$
0.000004	No ppt.	24 hr.	0.000235	$1:4.26 \times 10^6$
0.000003	No ppt.	No pink color	0.000176	$1:5.3 \times 10^6$
0.000002	No ppt.	No pink color	0.000117	

From the results tabulated above it appears that the proposed modification shortens considerably the time required for the precipitate of nickel glyoximine to become visible and also makes possible the detection of somewhat smaller concentrations of the nickel ion. Apparently this

is due to increased concentration of these ions by adsorption upon the precipitated silver cyanide. As evidence in favor of this view it may be noted that we found that precipitation of silver chloride in extremely dilute solutions of the nickel ion and dimethylglyoxime was equally effective in hastening formation of the pink nickel glyoximine, while precipitation of a positive colloid, such as aluminium hydroxide, had no effect whatever. Since both silver cyanide and silver cobalticyanide are white, the red nickel glyoximine is readily seen as a pink tint in the white precipitate and the delicacy of the reagent is increased.

**Oxidation of Cobaltocyanide to Cobalticyanide.**—When KCN is added to a solution of a cobalt salt, brownish white  $\text{Co(CN)}_2$  is precipitated and then redissolved to a greenish brown solution of  $\text{K}_4\text{Co(CN)}_6$ . When warmed this changes soon to a pale yellow color and the color change is frequently assumed in manuals of analysis to indicate completion of oxidation. When  $\text{AgNO}_3$  was added soon after the color change took place, we found that the solutions darkened and dark gray precipitates were formed, while solutions which had stood for several hours after cyanide was added did not darken and gave pure white precipitates. When one of the darkened solutions became distinctly opalescent, we inferred that some silver ion had been reduced by cobaltocyanide which was still present, according to the reaction



By adding silver nitrate solution to freshly prepared solutions of cobaltocyanide we found that this reaction takes place very slowly in cold but rapidly in hot solutions. When the silver nitrate was added dropwise the hot solutions first became lighter in color, then gradually turned orange and darkened until a gray precipitate was formed. If the addition of silver nitrate was stopped when the orange tint appeared, no precipitate formed, but the solution darkened on standing and became opalescent due to the formation of colloidal silver. This reaction was found to be regularly reproducible in solutions of cobaltocyanide not less than 0.005 *M*.

We next investigated the time required after the color change to complete the oxidation, taking the failure to form metallic silver as evidence that oxidation was essentially complete. Ten cc. portions of 0.1 *M*  $\text{CoSO}_4$  were treated in casseroles with just enough KCN to dissolve the precipitates, heated nearly to boiling and continuously rotated in the casseroles for a definite time to hasten oxidation. The solutions were diluted to 100 cc. with water at 85° and silver nitrate was added dropwise with vigorous stirring. All solutions which had been warmed less than five minutes gave colloidal silver or dark precipitates; those heated for at least this period did not darken and gave pure white precipitates. Presumably the time required increases with the amount of cobalt. Gauhe<sup>1</sup> showed

<sup>1</sup> *Loc. cit.*

that the oxidation of cobaltocyanide requires considerable time, but his experiments appear to have been forgotten.

**Detection of Nickel in Cobalt Salts.**—We next determined the minimum amount of nickel that could be detected in varying amounts of cobalt salts by our silver method and, for comparison, by two of the older methods, Treadwell's and that of Liebig-Gauhe.

*A. The Silver Method.*—Definite volumes of solutions of  $\text{NiSO}_4$  and  $\text{CoSO}_4$  of known concentration were measured from burets into a casserole, KCN was added until the precipitate just dissolved and the solution heated and rotated for five minutes after the change of color was noted. The solution was then diluted with water at  $85^\circ$  to 50 cc., 1 cc. of dimethylglyoxime solution was added, and then silver nitrate dropwise with constant stirring until a permanent precipitate was produced. The time required for the pink color of nickel glyoximine to appear was observed. In cases where the time exceeded one hour, observations were made at the end of twenty-four hours. The results appear in Table II.

TABLE II.

In each expt. 10 cc.  $\text{CoSO}_4$  0.0921 *M*, equivalent to 54.31 mg. Co was used.

$\text{NiSO}_4$ .		Ni mg.	Ratio Ni : Co.	Ratio Ni : $\text{H}_2\text{O}$ . Approx.	Results.
Vol. Cc.	Molar conc.				
2.0	0.0005	0.0587	1:925	$1:0.85 \times 10^6$	Ppt. pink immediate
1.5	0.0005	0.0440	1:1234	$1:1.14 \times 10^6$	Ppt. pink 4 min.
1.0	0.0005	0.0293	1:1851	$1:1.71 \times 10^6$	Ppt. pink 6 min.
4.5	0.0001	0.0264	1:2054	$1:1.89 \times 10^6$	Ppt. pink 10 min.
4.0	0.0001	0.0235	1:2314	.....	Ppt. pink 20 min.
3.5	0.0001	0.0205	1:2644	$1:2.44 \times 10^6$	Ppt. pink 30 min.
3.0	0.0001	0.0176	1:3085	.....	Ppt. pink 24 hrs.
2.5	0.0001	0.0137	1:3702	$1:3.65 \times 10^6$	Ppt. pink 24 hrs.

Taking the minimum amount of nickel, 0.0205 mg., which could be detected in cobalt within thirty minutes, we studied the effect of larger proportions of cobalt. The procedure and final total volumes were the same as in the preceding experiments. The results are shown in Table III. and indicate that the sensitiveness of the test is not appreciably impaired by the presence of large amounts of cobalt.

TABLE III.

$\text{CoSO}_4$ 0.0921 <i>M</i> . Cc.	Mg. [Co.	Ratio Ni : Co.	Results.
15	81.47	1:3966	Ppt. pink 30 min.
20	108.62	1:5288	Ppt. pink 30 min.
25	135.78	1:6610	Ppt. pink 30 min.
30	162.93	1:7932	Ppt. pink 30 min.

*B. The Treadwell Method.*—10 cc. portions of 0.0921 *M*  $\text{CoSO}_4$ , equivalent to 54.31 mg. Co, with varying small amounts of  $\text{NiSO}_4$  were warmed with concentrated ammonia until a clear solution was obtained, hydrogen peroxide was added, and the solutions were heated till excess of peroxide

and ammonia was removed, diluted to 50 cc., 1 cc. of dimethylglyoxime solution was added and the time required for the precipitate of nickel glyoximine to appear was observed. The results are given in Table IV.

TABLE IV.

NiSO <sub>4</sub> .					
Vol. Cc.	Conc. molar.	Mg. Ni.	Ratio Ni : Co.	Results.	
10	0.0005	0.293	1:185	Red ppt.	1 hr.
9	0.0005	0.264	1:206	Red ppt.	1 hr.
8	0.0005	0.235	1:231	Red ppt.	1 hr.
7	0.0005	0.205	1:264	Red ppt.	24 hrs.
5	0.0005	0.147	1:370	Red ppt.	24 hrs.
4	0.0005	0.117	1:462	Red ppt.	24 hrs.

Taking the minimum amount of nickel that could be detected in one hour, 0.235 mg., the effect of larger proportions of cobalt was studied. The procedure and final volume of solution were the same as in the experiments recorded in Table IV. The results are shown in Table V. Apparently this method is not very sensitive and fails when much cobalt is present, at least with the small amount of dimethylglyoxime which was used.

TABLE V.

Cc. CoSO <sub>4</sub> , 0.0921 M.	Mg. Co.	Ratio Ni : Co.	Results.
10	54.31	1:231	Red ppt. after 1 hr.
15	81.47	1:346	No ppt. after 1 hr.
20	108.62	1:462	No ppt. after 1 hr.

*C. The Liebig-Gauhe Method.*—10 cc. portions of CoSO<sub>4</sub>, 0.0921 M, with varying amounts of NiSO<sub>4</sub> were treated with a slight excess of KCN over that required to dissolve the precipitate, and heated and rotated until complete oxidation of the cobaltocyanide had taken place. They were then diluted to 50 cc. and freshly prepared sodium hypobromite solution was added. After the precipitate had flocculated, it was filtered off, washed, dissolved in dilute HCl, neutralized with ammonia and tested for Ni with dimethylglyoxime.

TABLE VI.

NiSO <sub>4</sub> , 0.0005 M.	Cc.	Mg. Ni.	Ratio Ni : Co.	Results.
	9	0.2641	1:206	Blk. ppt. Ni confirmed
	6	0.176	1:309	Blk. ppt. Ni confirmed
	3	0.088	1:617	Blk. ppt. Ni confirmed
	2	0.059	1:925	Blk. ppt. No Ni
	1	0.029	1:1850	Blk. ppt. No Ni
None	None			Blk. ppt. No Ni

This method appears able to detect 0.1 mg. nickel in a volume of 50 cc., but a confirmatory test must in every case be applied as the precipitate always contains cobaltic hydroxide if the hypobromite is added to a warm solution. Even if the temperature is kept low, Co(OH)<sub>3</sub> frequently precipitates.

Comparing the results of the three methods, the minimum amount of nickel detectable within one hour in a volume of 50 cc. is found to be:

Silver method.....	0.02 mg.
Treadwell method.....	0.23 mg.
Liebig-Gauhe method.....	0.09 mg.

These figures do not adequately convey the relative merits of the three methods, for it should be noted that the Liebig-Gauhe method requires a confirmatory test to make the result quite reliable; the Treadwell method failed to show the stated minimum amount of nickel when so little as 231 times as much cobalt as nickel was present; while the silver method appears to retain its full sensitiveness in presence of any amount of cobalt; moreover, it increases the sensitiveness of dimethylglyoxime about eight times and is able to detect within 24 hours less than 0.002 mg. of nickel in a volume of 50 cc.

### Summary.

1. A modified method of using dimethylglyoxime for detecting traces of nickel in cobalt salts is proposed which (a) avoids the use of large amounts of this rather costly reagent; (b) makes possible the detection of considerably smaller quantities of nickel than has been possible heretofore.

2. The sensitiveness of the test is shown to be unaffected by the presence of cobalt even in large quantities. The proposed method increases the ordinary sensitiveness of dimethylglyoxime about eight times and is capable of detecting about one-fifth the amount of nickel detectable by any of the previously known methods.

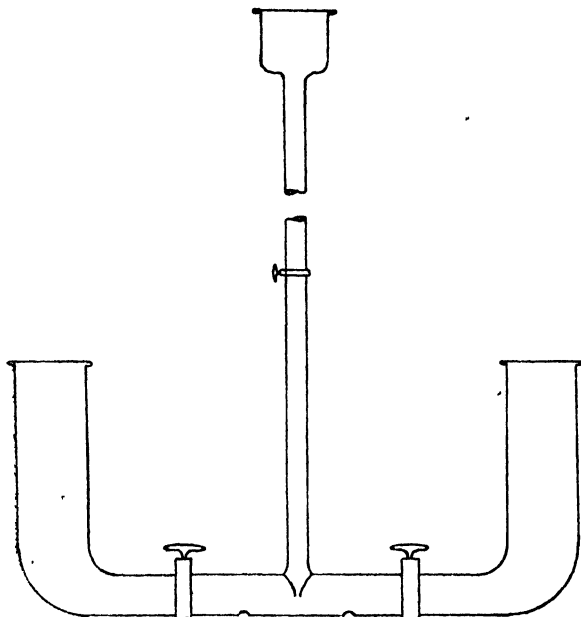
LAFAYETTE, IND.

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### NOTE.

**An Apparatus for Determining the Ions in a Solution.**—In the course of certain work which was being conducted in this laboratory, the following apparatus for the determination of the ions into which a solution dissociates was found to work very satisfactorily. The idea is similar to that expressed by Prof. Stieglitz in his *Qualitative Analysis*, Vol. I, page 70.

The apparatus is simple and readily constructed, consisting essentially of a U-tube with a means for closing the two arms and for introducing the substance to be tested into the lowest part of the tube. The center part is made by blowing into a piece of glass tubing of about one-half inch diameter a piece of ordinary sized tubing which has previously been drawn out into a fine jet, and fusing to the other end of this latter a thistle tube carrying a small bore stopcock. The large tube is ridged on either side of the jet tube to prevent lateral flowing of the introduced liquid. The side tubes, which are adapters, are connected with the center tube through large bore stopcocks. If the stopcocks are not handy, the side arms may be connected through rubber tubing bearing pinchcocks, although the use of this necessitates the running of two determinations since closing one side may force the liquid over into the other. Platinum electrodes are used.



In use the apparatus is kept in a bath of continually flowing cold water, the container for which is preferably of glass so that the electrolysis may be more readily watched. The tube is filled with an electrolyte of suitable concentration (0.25 *N* for 110 v. current) and of such a nature that it will not interfere with the results and the electrolysis started. Two cc. or more of the substance to be tested are introduced through the thistle tube and the ac-

tion allowed to run about one-half an hour when the side arms are closed and the contents tested.

For instance, with nitric acid as an electrolyte it can easily be shown after adding copper sulfate that the copper ion migrates to the cathode compartment and the sulfate ion to the anode, or, with calcium chloride that the calcium ion goes toward the cathode and the chloride ion toward the anode. With sodium hydrate as an electrolyte the complex ion of Fehling's solution, containing copper, or, the complex ion containing mercury of a solution of mercuric sulfide in sodium hydrate, probably  $\text{HgS}^{--}$ , migrates toward the anode. It was also used in the determination of the charge on inorganic colloids.

RALPH W. G. WYCKOFF.

HOBART COLLEGE LABORATORIES,  
GENEVA, N. Y.

[CONTRIBUTIONS FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY,  
No. 270.]

## STUDIES ON CATALYSIS. I. THE ADDITION COMPOUNDS OF ESTERS WITH ORGANIC ACIDS.<sup>1</sup>

BY JAMES KENDALL AND JAMES ELIOT BOOGE.

Received May 29, 1916.

CONTENTS.—1. Introduction. Purpose and Scope of Investigation. 2. Review of Previous Work: (a) The Mechanism of Acid Catalysis of Ester Hydrolysis; (b)

<sup>1</sup> For previous papers on addition compound formation see *THIS JOURNAL*, 36, 1222, 1722, 2498 (1914); 37, 149 (1915); 38, 1309 (1916).



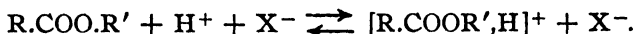
Addition Compound Formation in Systems Ester-Acid. 3. Experimental Procedure. 4. Experimental Data. 5. Relative Stability of Addition Compounds. 6. Compound Formation a General Phenomenon. 7. Structure of Addition Compounds Isolated. 8. Summary.

### 1. Introduction. Purpose and Scope of Investigation.

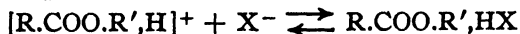
Few reactions have been more carefully studied than the catalysis of ester hydrolysis by acids. We have at our disposal, from among the multitude of experimental facts recorded, data for all the possible range of conditions—variation of the ester, variation of the acid, variation of temperature, variation of the concentration of ester, of acid, and of water. This being so, it is only natural that there should also exist an accumulation of hypotheses regarding the nature and the mechanism of the reaction. The strange thing is that, in spite of all, few reactions are still so little understood.

The main reason for this unfortunate state of affairs is that theories have always been thrust far in advance of facts, so far indeed that they have often lost touch of them altogether. The experimental data have been systematically overworked in their task of supporting unwieldy masses of premature speculation.

As one possible explanation of the catalysis of ester hydrolysis by acids, the theory of intermediate addition compounds has been advanced, and appears to hold the field at present. The great majority of chemists who have, in recent years, attempted to elucidate the mechanism of the reaction have regarded as the *first step* in the hydrolysis the addition of the acid to the ester to form an oxonium salt.<sup>1</sup> Although a number of papers do not give this first step definitely, the formulation most favored is



The formation of this complex ester-hydrogen-ion  $[\text{R.COO.R}',\text{H}]^+$  necessitates the further assumption that the undissociated compound as given by the equilibrium



must also be present. Until now only a single compound of the suggested type has definitely been isolated. We have therefore no direct proof that such compound formation is a *general phenomenon* in systems of the type ester-acid, and upon this assumption the whole theory rests. Consequently it seemed to the authors especially desirable to investigate *systematically* the general behavior of ester-acid mixtures with respect to compound formation.

The results of this investigation were very gratifying, as thirteen compounds of the type (ester)<sub>m</sub>, (acid)<sub>n</sub> were isolated. Moreover it may be

<sup>1</sup> In this paper the terms "addition compound" and "oxonium salt" are synonymous.

deduced that any ester,  $R.COOR'$ , will combine directly with any acid,  $HX$ , to a greater or less amount, and the main factors governing the extent of addition compound formation are also made clear. By direct isolation of these compounds, which have heretofore merely been *assumed* to exist, strong support is thus given to the theory of intermediate oxonium salt formation in the catalytic hydrolysis of esters by acids.

## 2. Review of Previous Work.

A brief outline of some of the previous work in this field will aid in the consideration of our results.

(a) **The Mechanism of Acid Catalysis of Ester Hydrolysis.**—Various theories have been formulated to explain this phenomenon. The more prominent may be grouped into three classes.

**Class I. Assumption: The Catalyst Acts by its Mere Presence.**—The old view of catalysis was that the acid (hydrogen ion) acted in some mysterious manner, the reaction obediently proceeding with increased velocity.

A rational modification of this view has recently been advanced by Lewis<sup>1</sup> and coworkers. It is assumed that the (hydrated) methyl acetate molecule absorbs quanta of radiation in the infra-red region, sent out by the (hydrated) hydrogen ion, the consequent addition of energy to the ester molecule inducing great instability or chemical activity. This view is appealing in its simplicity but has not been sufficiently developed experimentally to judge whether it can explain the complicated relations holding between velocity of hydrolysis and concentration of the reacting substances. Moreover, it simply postulates the *driving force* which increases the velocity of the reaction without accounting for the mechanism or stages in which the reaction takes place.<sup>2</sup>

**Class II. Assumption: Direct Ionization of Organic Compounds.**—This was the natural outgrowth of the too enthusiastic application of the ionic theory. Direct ionization of the ester to  $R.COO^-$  and  $R'^+$  was postulated by Zengelis<sup>3</sup> and to  $RCO^+$  and  $OR'^-$  by Euler.<sup>4</sup> Increased concentration of hydrogen ion would tend to remove one of the ions in each case, accelerating the hydrolysis of the ester. The decreased concentration of hydroxide ion would, however, simultaneously have the opposite effect. Due to the lack of verification of such ionizations and to the incorrect quantitative results<sup>5</sup> to which they lead, these views have been discarded.

<sup>1</sup> *J. Chem. Soc.*, 105, 2330 (1914); 107, 233 (1915); 109, 55, 67 (1916).

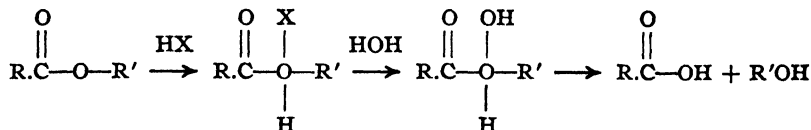
<sup>2</sup> In any metathesis there are necessarily but two possible mechanisms—either decomposition of  $AB$  and  $CD$  followed by combination of the parts, or intermediate combination to  $AB.CD$  followed by decomposition in another way. Both of these views have been advanced in ester hydrolysis (See II and III).

<sup>3</sup> "On Chemical Affinity," Athens, 1896, *Ber.*, 34, 198 (1901).

<sup>4</sup> *Z. physik. Chem.*, 36, 640 (1901).

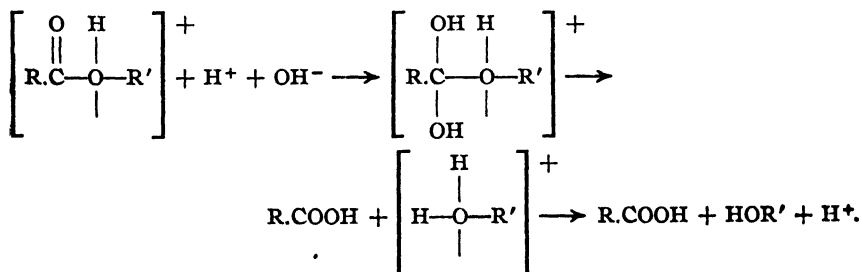
<sup>5</sup> Stieglitz, *Am. Chem. J.*, 39, 404, 423 (1908).

**Class III. Assumption: Intermediate Addition Compounds are Formed.**—Kastle,<sup>1</sup> in a paper read before the A. A. A. S. in 1896, first suggested the possibility that an "addition product" of the ester and catalyzing acid might be formed. His formulation of the reaction



is undoubtedly incorrect, assuming as it does greater concentration of oxonium base in a more strongly acid solution. Bredig<sup>2</sup> suggested, in 1903, and again in 1904, that the complex ion  $[\text{R.COO.R'}, \text{H}]^+$  may be active in the hydrolysis of esters. Lapworth, in 1904 (Mellor's "Statics and Dynamics," p. 289), gave a more complete formulation of the hydrolysis in the presence of an acid. This view has likewise been severely criticized and has no experimental evidence in its support.<sup>3</sup> Acree,<sup>4</sup> Rosanoff,<sup>5</sup> Falk and Nelson,<sup>6</sup> and numerous other chemists have assumed the formation of intermediate addition compounds, the last named authors applying the electron conception of valence, without however considering the subject quantitatively.

Stieglitz<sup>7</sup> has treated the whole problem from a quantitative standpoint, starting from the fact that a possible mechanism for the catalysis is



From this there is deduced the expression for the velocity of hydrolysis

$$\frac{dx}{dt} = K_s \cdot C_{\text{ester}} \cdot C_{\text{H}^+} \cdot C_{\text{H}_2\text{O}}$$

This was at the time supposed to represent the experimental facts, but in the light of more recent work becomes a rough approximation only. Thus

<sup>1</sup> Stieglitz, *Am. Chem. J.*, 39, 421 (1908).

<sup>2</sup> *Z. Electrochem.*, 9, 118 (1903); 10, 586 (1904).

<sup>3</sup> Stieglitz, "International Congress of Arts and Sciences" at St. Louis, 4, 278 (1904); *Am. Chem. J.*, 39, 424 (1908).

<sup>4</sup> *Am. Chem. J.*, 48, 352 (1912).

<sup>5</sup> *This Journal*, 35, 173 (1913).

<sup>6</sup> *Ibid.*, 37, 1732 (1915).

<sup>7</sup> *Am. Chem. J.*, 39, 29, 60 (1908).

it has been demonstrated within the last few years that the velocity,  $-dx/dt$ , increases *more rapidly* than  $C_{\text{ester}}$  or  $C_{\text{H}^+}$ , *i. e.*, increase in the concentration of water (dilution of the solution) causes more of a retardation than that calculated by the law of mass action.<sup>1</sup>

To explain the abnormal acceleration of hydrolysis with increase of  $C_{\text{H}^+}$  several theories have been advanced, notably the theory of the negative catalytic effect of water and the theory that the undissociated acid molecules,  $\text{HX}$ , are also catalytically active. These theories, together with the bearing of the results of the present paper upon them, will be examined in a subsequent communication.

From the foregoing discussion it will be apparent that the catalytic activity of acids has not been satisfactorily explained in a quantitative way—and that this can scarcely be expected until the complete mechanism of the reaction is rigorously established.

(b) **Addition Compound Formation in Systems Ester-Acid.**—The *experimental* evidence of the existence of such compounds is very unsatisfactory.

Lewis has recently<sup>2</sup> advanced the hypothesis that an *ester-water* compound  $\text{R.COO.R'}. \text{HOH}$  is active in hydrolysis. Absorption in the infra-red region is the only evidence brought forward that such compounds exist. A compound of this type has never been isolated and moreover the work of Rivett<sup>3</sup> indicates that such a compound does not exist, to any appreciable extent, in an aqueous solution of ethyl acetate. From his results for the freezing-point depression of water by this ester, *recalculated to weight concentrations*,<sup>4</sup> it is seen that the depression is exactly linear; hence no combination, or at most only a minute trace, occurs.

On the other hand, the results of the present paper definitely establish the existence of binary compounds, *ester-acid*. Previous evidence on this question is almost entirely indirect. Thus the increasing molecular conductivity with increase of concentration of esters dissolved in liquid hydrogen halides is taken as being due to combination followed by ionization.<sup>5</sup> Many classes of organic oxygen compounds, as alcohols, acids, phenols, ketones, etc., form oxonium salts with various inorganic and organic acids; esters would be expected to form analogous compounds. The validity of such indirect evidence is, however, always open to suspicion and cannot have the same weight as the actual isolation of the compounds in question.

<sup>1</sup> Taylor, *Meddel. K. Vetensk. Nobelinst.*, 2, Nos. 34, 35, 37 (1913); Dawson and Powis, *J. Chem. Soc.*, 103, 2139 (1913); Lewis, *Ibid.*, 109, 67 (1916).

<sup>2</sup> *Ibid.*, 109, 80 (1916).

<sup>3</sup> *Z. physik. Chem.*, 80, 547 (1912).

<sup>4</sup> Noyes and Falk, *THIS JOURNAL*, 32, 1013 (1910).

<sup>5</sup> Walker, McIntosh and Archibald, *J. Chem. Soc.*, 85, 1100 (1904).

**Direct Evidence.**—Baeyer and Villiger<sup>1</sup> obtained "compounds" of  $\text{H}_3\text{Fe}(\text{CN})_6$  with ethyl acetate, ethyl benzoate and diethyl oxalate and of  $\text{H}_4\text{Fe}(\text{CN})_6$  with diethyl oxalate. Some uncertainty is introduced into the assumption that these are actually compounds by the work of McIntosh,<sup>2</sup> who conclusively proved that Baeyer and Villiger's "compounds" of ether and of acetone with  $\text{H}_4\text{Fe}(\text{CN})_6$  are in reality solid solutions. The only definite isolation of oxonium compounds of an ester with an acid is given by Maass and McIntosh,<sup>3</sup> who completely investigated the system, ethyl acetate-hydrogen chloride. The compounds formed were  $\text{CH}_3\text{COO.C}_2\text{H}_5\text{HCl}$ ;  $\text{CH}_3\text{COO.C}_2\text{H}_5\text{HCl}$ ; and  $2\text{CH}_3\text{COO.C}_2\text{H}_5\text{HCl}$ .

### 3. Experimental Procedure.

The complete examination of 22 ester-acid systems has been accomplished by the freezing-point method previously described. A number of mixtures of known composition are successively prepared for a binary system and the freezing point, *i. e.*, the temperature at which a minimum (negligible) amount of solid is in *equilibrium* with the liquid phase, is taken for each mixture. A series of such points determines the temperature-composition curve. In the diagram so obtained a break in the curve indicates a change in the solid phase crystallizing out. A maximum point indicates a compound, the position of the maximum with reference to the molecular composition axis gives the formula of the compound and the slope of the curve around the maximum indicates the extent of dissociation of the compound into its components, here ester and acid. For further details previous papers of this series should be consulted.<sup>4</sup>

The behavior of systems of the type  $\text{R.COO.R}'\text{-HX}$  will be dependent upon the character of the three radicals R, R' and X.<sup>5</sup> In order to make our conclusions as general as possible, all three radicals have been widely varied in the different systems examined.

The acids, HX, employed were trichloroacetic (the strongest of the simple organic acids), chloroacetic (a typical transition acid), and acetic (a typical weak acid). Esters of both monobasic and dibasic aliphatic and aromatic acids were chosen, the acids varying in strength from acetic to oxalic. The third radical, R', was varied by working with ethyl, methyl, benzyl, phenyl, and  $\alpha$ - and  $\beta$ -naphthyl esters. The following table gives the dissociation constants of the acids used and of the acids from which the esters were derived:

<sup>1</sup> *Ber.*, **34**, 2692 (1901).

<sup>2</sup> *THIS JOURNAL*, **30**, 1097 (1908).

<sup>3</sup> *Ibid.*, **34**, 1288 (1912).

<sup>4</sup> Kendall, *Ibid.*, **36**, 1225 (1914).

<sup>5</sup> Kendall and Gibbons, *THIS JOURNAL*, **37**, 159 (1915).

TABLE I.—DISSOCIATION CONSTANTS OF ACIDS.<sup>1</sup>

	100 K.		100 K.
Trichloroacetic.....	121.0	Salicylic.....	0.102
Monochloroacetic.....	0.155	Benzoic.....	0.0060
Acetic.....	0.0018	$\alpha$ -Toluic.....	0.00556
		<i>p</i> -Toluic.....	0.00515
Oxalic.....	10.0	Cinnamic.....	0.00355
Malonic.....	0.158	Anisic.,.....	0.0032
Succinic.....	0.00665	Terephthalic.....	0.015 (approx.)

From previous work on binary mixtures<sup>2</sup> the following relations are to be expected:

(1) **Varying X.**—Strong acids should give marked compound formation, with the possibility of isolating the compounds; weak acids, on the other hand, should exhibit less combination.

(2) **Varying R.**—Compound formation should be less for derivatives of strong than for those of weak acids. Making R more "negative" (as in passing from ethyl acetate to ethyl benzoate) should decrease the amount of combination.

(3) **Varying R'.**—As R' becomes more "negative" (for example, as we pass from phenyl benzoate to ethyl benzoate) the ester should exhibit less compound formation with acids. Thus the "basic properties" (tendency to form onium compounds) of the ester oxygen atoms should be repressed by the proximity of "negative" groups.

These expectations were indeed realized, as will be shown in Section 5. The views in regard to the relative stability of oxonium compounds put forward in previous papers of this series have thus received further confirmation.

**Measurement of Temperatures.**—Above  $-35^{\circ}$  several mercury thermometers with convenient ranges of scale, graduated in tenths, were used. These were calibrated as usual at  $0^{\circ}$  and  $100^{\circ}$  and also compared with certified thermometers. The toluene thermometer employed for temperatures below  $-35^{\circ}$  was accurate down to  $-35^{\circ}$  by calibration with a certified mercury thermometer. At  $-78.2^{\circ}$  ( $\text{CO}_2$ -alcohol paste) and  $-82.8^{\circ}$  (m. p. of pure ethyl acetate)<sup>3</sup> it was still accurate to within  $\pm 1^{\circ}$ .<sup>4</sup>

The melting points given are corrected as usual for exposed stem. The stem correction for the toluene thermometer was so large ( $7-8^{\circ}$ ) that it was deemed safer to determine it directly than to use the coefficient of expansion of toluene, which varies with the temperature. The stem

<sup>1</sup> Ostwald, *Z. physik. Chem.*, **3**, 377, 418 (1889).

<sup>2</sup> Kendall, *Loc. cit.*

<sup>3</sup> Guttman, *THIS JOURNAL*, **29**, 345 (1907).

<sup>4</sup> A greater accuracy at these temperatures is very difficult to obtain. See Guttman, *Loc. cit.*, and Beckmann and Waentig, *Z. anorg. Chem.*, **69**, 17 (1910).

corrections found experimentally at a number of temperatures were plotted and used in correcting observed melting points between  $-35^{\circ}$  and  $-100^{\circ}$ .

The temperatures given later in the tables may be taken as having the following degree of accuracy:

Temperatures from $150^{\circ}$ to $100^{\circ}$	Possible error $0.2-0.5^{\circ}$
Temperatures from $100^{\circ}$ to $-10^{\circ}$	Possible error $0.1-0.2^{\circ}$
Temperatures from $-10^{\circ}$ to $-35^{\circ}$	Possible error $0.2-0.5^{\circ}$
Temperatures from $-35^{\circ}$ to $-100^{\circ}$	Possible error $1.0-2.0^{\circ}$ (usually $\pm 1^{\circ}$ )

A somewhat greater comparative accuracy for points on the same curve was attained, as is evidenced also by the smoothness of the curves.

For cooling below  $-20^{\circ}$  carbon dioxide snow and acetone were used, and for temperatures below  $-80^{\circ}$ , liquid air. Supercooling of the mixtures was quite general. To induce a compound to crystallize when no solid was available for seeding, it was often necessary to cool the mixture some  $50^{\circ}$  below the freezing point (to a glass), and allow it to warm slowly, vigorously scratching the walls of the tube. After several hours' repetition of this procedure the compound could usually be persuaded to crystallize out.

In all cases the melting point was determined by warming the partially frozen mixture very slowly and observing the temperature at which the last traces of crystals were *just in equilibrium* with the liquid, *i. e.*, the true temperature of incipient freezing. Points on a curve could be duplicated with a separate mixture of the same composition to within the limits of experimental error. Likewise even after it had stood for several days with the exclusion of moisture a given mixture exhibited the same melting point as immediately after mixing. This proves that the formation of the addition compound is not a time reaction, but is practically instantaneous even at temperatures below  $-50^{\circ}$ .

In the following tables, as elsewhere in the paper, the composition of every mixture is expressed in *molecular* percentages.

#### 4. Experimental Data.

**A. Systems with Trichloroacetic Acid.**—Trichloroacetic acid, after prolonged desiccation over sulfuric acid, *in vacuo*, gave a melting point of above  $58^{\circ}$  ( $55^{\circ}$  in literature).

**1. Ethyl Acetate.**—The ethyl acetate used was a pure commercial sample, washed with water and carefully fractionated after standing over calcium chloride. It froze at a constant temperature of  $-83^{\circ} \pm 1^{\circ}$ . The compound,  $\text{CH}_3\text{COO.C}_2\text{H}_5\text{CCl}_3\text{COOH}$ , was obtained, crystallizing in large glistening plates, melting at  $-27.5^{\circ}$ .

(a) Solid Phase,  $\text{CH}_3\text{COO.C}_2\text{H}_5$ .

Per cent. ester.....	100	95.5
Temp.....	$-83.0$	$-88.0$

(b) Solid Phase,  $\text{CH}_3\text{COO.C}_2\text{H}_5\text{CCl}_3\text{COOH}$ .

Per cent. ester.....	87.1	78.9	70.5	59.9	50.0	47.8	45.3
Temp.....	-70.5	-53.0	-42.0	-32.5	-27.5	-28.1	-28.9

(c) Solid Phase,  $\text{CCl}_3\text{COOH}$ .

Per cent. ester.....	40.1	32.7	24.6	17.6	8.5	0	
Temp.....	-18.3	10.7	30.4	42.8	52.3	58.8	

2.  $\alpha$ -Naphthyl Acetate.—This ester was prepared from acetyl chloride and  $\alpha$ -naphthol, the product being decolorized with animal charcoal, recrystallized three times from alcohol and finally from  $\text{CCl}_4$ . The compound  $\text{CH}_3\text{COO.C}_{10}\text{H}_7\text{CCl}_3\text{COOH}$ , crystallizing in prismatic needles and melting at  $10.7^\circ$ , was isolated.

(a) Solid Phase,  $\text{CH}_3\text{COO.C}_{10}\text{H}_7$ .

Per cent. ester.....	100	90.4	82.3	76.0	69.6	64.0	58.6
Temp.....	44.8	40.0	34.8	29.7	23.6	16.5	7.5

(b) Solid Phase,  $\text{CH}_3\text{COO.C}_{10}\text{H}_7\text{CCl}_3\text{COOH}$ .

Per cent. ester.....	54.3	50.1	46.2	40.7	35.4		
Temp.....	10.0	10.7	10.2	8.0	6.0		

(c) Solid Phase,  $\text{CCl}_3\text{COOH}$ .

Per cent. ester.....	30.0	23.3	15.5	8.1	0		
Temp.....	21.0	33.5	44.5	51.9	58.0		

3.  $\beta$ -Naphthyl Acetate.—This ester, after preparation from  $\beta$ -naphthol and acetic anhydride, was, with difficulty, purified by repeated rapid recrystallization from alcohol. The work was carried out below  $0^\circ$  to retard hydrolysis. An equimolecular compound with a rather high melting point ( $66.3^\circ$ ) was obtained, crystallizing in thin, oblong plates. (See Curve V, Fig. 1.)

(a) Solid Phase,  $\text{CH}_3\text{COO.C}_{10}\text{H}_7$ .

Per cent. ester.....	100	89.9	82.4		
Temp.....		68.5	63.9	59.4	

(b) Solid Phase,  $\text{CH}_3\text{COO.C}_{10}\text{H}_7\text{CCl}_3\text{COOH}$ .

Per cent. ester.....	71.1	65.2	60.1	55.1	50.0
Temp.....	55.5	60.9	63.6	65.4	66.3
Per cent. ester.....	45.6	43.0	38.1	32.4	24.5
Temp.....	65.7	64.8	62.3	57.7	48.7

(c) Solid Phase,  $\text{CCl}_3\text{COOH}$ .

Per cent. ester.....	16.1	8.6	0		
Temp.....	43.8	51.5	58.2		

4. Ethyl Benzoate.—A pure sample was fractionated and the portion boiling between  $208.3^\circ$  and  $208.6^\circ$  used. This gave a melting point of  $-32.7^\circ$  (not previously determined). A second crystalline form (m. p.  $-40^\circ$ ) was also found to exist. (Compare methyl benzoate.) A compound,  $\text{C}_6\text{H}_5\text{COO.C}_2\text{H}_5\text{CCl}_3\text{COOH}$ , crystallizing in sheaves of needles, was isolated; m. p.  $-23.4^\circ$ .



(a) Solid Phase,  $C_6H_5.COO.C_2H_5$ .

Per cent. ester.....	100	87.7	78.8
Temp.....	—32.7	—38.4	—45.0

(b) Solid Phase,  $C_6H_5.COO.C_2H_5.CCl_3.COOH$ .

Per cent. ester.....	71.0	64.4	61.1	54.4	50.0	47.3	45.2
Temp.....	—38.5	—31.6	—28.5	—24.7	—23.4	—23.5	—24.0

(c) Solid Phase,  $CCl_3.COOH$ .

Per cent. ester.....	40.7	35.3	29.8	24.4	19.7	14.0	7.2	0
Temp.....	—10.1	6.0	20.0	30.5	38.5	46.2	53.2	58.7

**5. Methyl Benzoate.**—The methyl benzoate was prepared as usual from benzoic acid and absolute methyl alcohol by saturation with hydrogen chloride. The fraction boiling constantly at  $197.8^\circ$  gave a melting point of  $-12.3^\circ$  (not previously determined). A metastable crystalline form also exists with m. p.  $-13.7^\circ$ . This gives rise to a second melting-point curve paralleling that of the stable form. An equimolecular compound (also existing in two crystalline modifications, m. p.  $-10.6^\circ$  and  $-8.8^\circ$ , both crystallizing in needles) was isolated. (See Curve II, Fig. 1.)

(a) Solid Phase,  $C_6H_5.COO.CH_3$ .

## Metastable Form.

Per cent. ester..	100	95.7	94.0	92.9
Temp.....	—13.7	—15.0	—16.3	—17.0

## Stable Form.

Per cent. ester..	100	94.0	92.3	90.5	87.2	83.4	78.0	75.0
Temp.....	—12.3	—14.7	—15.4	—16.5	—18.6	—21.5	—25.5	—28.5

(b) Solid Phase,  $C_6H_5.COO.CH_3.CCl_3.COOH$ .

Per cent. ester..	72.7	70.7	66.3	65.4	62.5	
Temp.....	—25.5	—23.3	—18.6	—17.9	—15.3	
Per cent. ester..	60.0	55.8	52.5	50.0	47.7	44.3
Temp.....	—13.1	—10.5	—9.3	—8.8	—9.2	—10.1

(c) Solid Phase,  $CCl_3.COOH$ .

Per cent. ester..	43.2	39.7	36.2	31.4	26.2	20.2	14.3	8.2	0
Temp.....	—15.6	—4.8	4.2	15.9	26.4	36.5	44.2	50.9	57.5

**6. Benzyl Benzoate.**—By fractionation under reduced pressure benzyl benzoate of m. p.  $18.3^\circ$  was obtained. The compound  $C_6H_5.COO.CH_2.C_6H_5.CCl_3.COOH$ , crystallizing in clusters of needles (m. p.  $11.9^\circ$ ), was isolated.

(a) Solid Phase,  $C_6H_5.COO.CH_2.C_6H_5$ .

Per cent. ester.....	100	90.8	80.9	76.1	74.8	72.1	71.3	69.9	67.5
Temp.....	18.3	15.4	13.3	6.8	6.4	4.5	4.0	2.0	—1.0

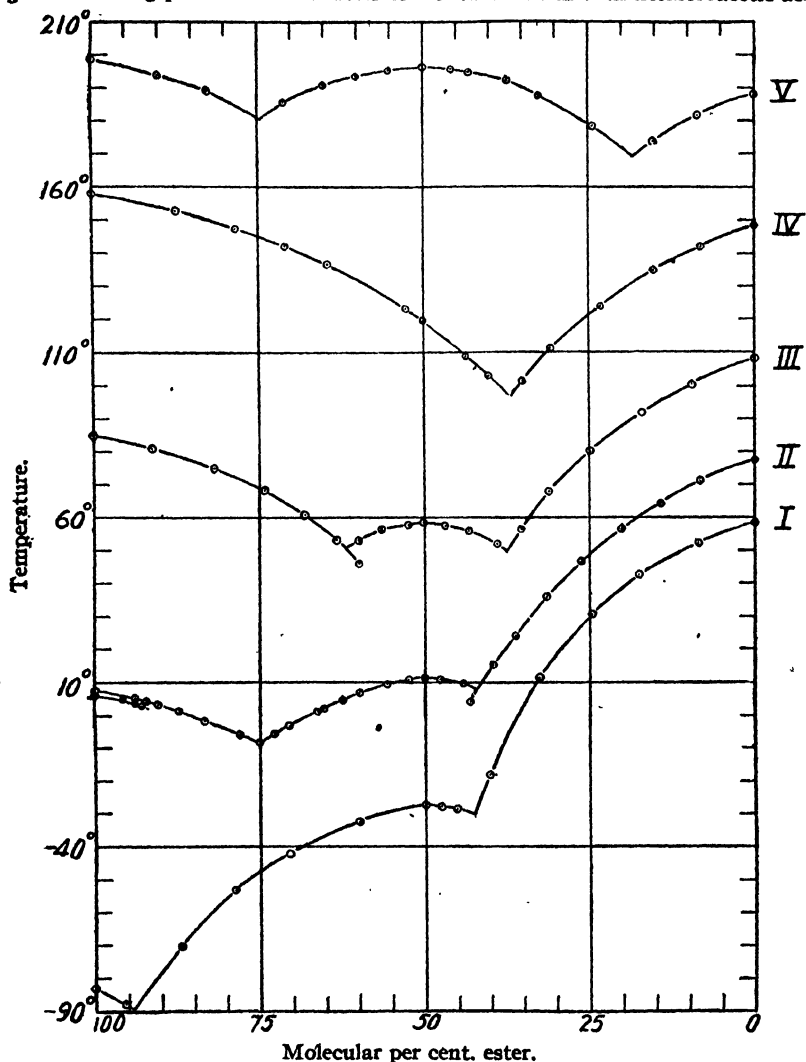
(b) Solid Phase,  $C_6H_5.COO.CH_2.C_6H_5.CCl_3.COOH$ .

Per cent. ester.....	69.8	67.5	63.1	57.9	54.1	50.2	48.8	44.6	39.8
Temp.....	—1.5	1.5	6.5	9.5	10.9	11.9	11.8	11.5	10.2

(c) Solid Phase,  $CCl_3.COOH$ .

Per cent. ester.....	35.6	30.0	25.2	19.7	13.8	6.3	0
Temp.....	10.0	21.6	30.3	38.7	45.5	53.1	57.9

Fig. 1.—Freezing-point curves of esters of monobasic acids with trichloroacetic acid.



- I. Ethyl acetate (scale correct).  
 II. Methyl benzoate (subtract 20°).  
 III. Methyl cinnamate (subtract 50°).  
 IV. Phenyl benzoate (subtract 90°).  
 V.  $\beta$ -Naphthyl acetate (subtract 130°).

**7. Methyl Anisate.**—Methyl anisate was prepared from anisic acid, absolute methyl alcohol and sulfuric acid by refluxing. The product, recrystallized from methyl alcohol by cooling to 0°, gave a m. p. of 48.3° (45–46° in literature). A compound,  $\text{CH}_3\text{O.C}_6\text{H}_4.\text{COO.CH}_3.\text{CCl}_3\text{COOH}$ , crystallizing in small, glittering plates, m. p.  $-6.3^\circ$ , was isolated. This compound also crystallized in a metastable form of lower melting point.

(a) Solid Phase,  $\text{CH}_3\text{O.C}_6\text{H}_4.\text{COO.CH}_3$ .

Per cent. ester.....	100	91.4	84.7	78.8	73.1	67.2	61.6	58.2	56.2
Temp.....	48.3	43.7	39.2	34.0	27.9	19.5	9.5	0.0	-5.5

(b) Solid Phase,  $\text{CH}_3\text{O.C}_6\text{H}_4.\text{COO.CH}_3, \text{CCl}_3.\text{COOH}$ .

Per cent. ester.....	54.7	50.0	44.9	40.6
Temp.....	-7.4	-6.3	-7.0	-9.5

(c) Solid Phase,  $\text{CCl}_3.\text{COOH}$ .

Per cent. ester.....	37.6	34.6	29.5	22.7	16.5	9.2	0
Temp.....	-6.5	5.0	17.0	31.5	41.1	50.6	58.1

**8. Methyl Cinnamate.**—Methyl cinnamate (prepared by passing hydrogen chloride into a solution of cinnamic acid in absolute methyl alcohol) was recrystallized from alcohol with the addition of water until turbid, followed by cooling on ice. The ester showed no test for chlorine and melted at  $34.7^\circ$  ( $33^\circ$  in literature). With trichloroacetic acid an equimolecular compound, crystallizing in slender needles, was obtained. That the double bond has nothing to do with the formation of this compound is evidenced by the fact that HCl does *not* add on *permanently* during the preparation of the ester.<sup>1</sup> (See Curve III, Fig. 1.)

(a) Solid Phase,  $\text{C}_6\text{H}_5.\text{CH}:\text{CH}.\text{COO.CH}_3$ .

Per cent. ester.....	100	91.2	81.8	74.3	68.0	63.2	59.9
Temp.....	34.7	30.8	25.0	18.4	10.9	3.3	-3.7

(b) Solid Phase,  $\text{C}_6\text{H}_5.\text{CH}:\text{CH}.\text{COO.CH}_3, \text{CCl}_3.\text{COOH}$ .

Per cent. ester.....	59.9	56.5	52.4	50.2	46.9	43.2	38.0
Temp.....	3.2	6.4	7.9	8.5	7.7	6.0	1.9

(c) Solid Phase,  $\text{CCl}_3.\text{COOH}$ .

Per cent. ester.....	35.2	31.0	24.9	17.1	9.4	0
Temp.....	6.5	17.8	30.0	41.9	50.4	58.3

**9. Methyl *p*-Toluate.**—The ester was prepared from *p*-toluic acid dissolved in absolute methyl alcohol and saturated with hydrogen chloride. After several recrystallizations from diluted methyl alcohol the ester melted at  $33.2^\circ$  ( $32^\circ$  in literature). A compound crystallizing in rectangular plates, m. p.  $9^\circ$ , was obtained.

(a) Solid Phase,  $\text{CH}_3\text{C}_6\text{H}_4.\text{COO.CH}_3$ .

Per cent. ester.....	100	86.7	81.0	75.5	68.4	62.1
Temp.....	33.2	28.8	25.4	21.1	13.6	4.7

(b) Solid Phase,  $\text{CH}_3\text{C}_6\text{H}_4.\text{COO.CH}_3, \text{CCl}_3.\text{COOH}$ .

Per cent. ester.....	57.5	53.0	50.0	46.4	42.2	37.7
Temp.....	6.0	8.2	9.0	8.6	7.1	3.4

(c) Solid Phase,  $\text{CCl}_3.\text{COOH}$ .

Per cent. ester.....	33.8	26.4	16.8	8.9	0
Temp.....	11.0	28.6	43.1	52.0	59.2

<sup>1</sup> The addition of HCl at the double bond would give a stable saturated compound not again decomposed by addition of water as are the oxonium compounds. Also here, as in previous work, the cinnamic acid behaves normally with respect to stability of the compound, etc.—the double bond having no apparent effect. No compound could be isolated with chloroacetic acid. (See System 20, below.)

**10. Phenyl Benzoate.**—The phenyl benzoate was prepared by the Schotten-Baumann reaction and purified by several recrystallizations from alcohol. No compound could be isolated, but the slope of the curve shows much compound formation in the liquid phase. (See Curve IV, Fig. 1.)

(a) Solid Phase,  $C_6H_5.COO.C_6H_5$ .

Per cent. ester.....	100	87.4	78.4	70.9	64.5	52.7	50.2	43.8	40.3
Temp.....	67.8	62.8	57.3	52.1	46.7	33.0	29.6	19.0	13.2

(b) Solid Phase,  $CCl_3.COOH$ .

Per cent. ester.....	35.0	30.7	23.3	15.2	8.0	0			
Temp.....	11.5	21.0	33.7	44.7	52.1	58.5			

**11. Phenyl Salicylate.**—A commercial specimen of satisfactory m. p. was employed. Although no compound could be isolated, yet the form of the curve (see later) again indicated much combination in the liquid phase.

(a) Solid Phase,  $HO.C_6H_4.COO.C_6H_5$ .

Per cent. ester.....	100	95.1	87.9	84.3	80.4	76.3			
Temp.....	41.9	39.9	36.4	34.4	32.1	29.5			
Per cent. ester.....	72.4	67.7	64.7	58.6	50.3				
Temp.....	27.5	23.8	21.6	15.8	8.0				

(b) Solid Phase,  $CCl_3.COOH$ .

Per cent. ester.....	19.8	14.2	8.2	0					
Temp.....	39.5	45.4	51.7	57.9					

**12. Diethyl Succinate.**—A specimen from a well-known manufacturer, after fractionation, gave a m. p. of  $-20.8^\circ$ , identical with that given in the literature. The central portion of the curve could not be completed, as mixtures in this region refused to crystallize even after standing for some time in liquid air. However, the form of the curve (as far as it could be traced) leaves little reason for doubt that the compound  $C_2H_4(COO.C_2H_5)_2, 2CCl_3.COOH$  is present in the liquid mixture (compare dimethyl succinate below). (See Curve III, Fig. 2.)

(a) Solid Phase,  $C_2H_4(COO.C_2H_5)_2$ .

Per cent. ester.....	100	90.8	82.7	75.1	67.3	59.8			
Temp.....	$-20.8$	$-23.3$	$-26.5$	$-30.2$	$-35.6$	$-44.0$			

(b) Solid Phase,  $CCl_3.COOH$ .

Per cent. ester.....	30.9	28.1	23.9	19.5	14.5	9.9	0		
Temp.....	$-26.0$	$-9.1$	9.5	25.5	38.2	47.1	58.3		

**13. Dimethyl Succinate.**—This ester was prepared by the usual method. The compound isolated,  $C_2H_4(COO.CH_3)_2, 2CCl_3.COOH$ , crystallized in slender prisms, m. p.  $8.0^\circ$ . (See Curve IV, Fig. 2.)

(a) Solid Phase,  $C_2H_4(COO.CH_3)_2$ .

Per cent. ester.....	100	91.5	82.0	76.2	69.9	64.5	60.3		
Temp.....	18.2	15.4	10.7	6.8	1.4	$-4.2$	$-9.8$		

(b) Solid Phase,  $C_2H_4(COO.CH_3)_2, 2CCl_3.COOH$ .

Per cent. ester.....	56.9	52.5	50.2	47.5	44.9	43.4	40.3
Temp.....	-13.4	-6.9	-3.3	-1.0	1.9	2.7	5.5
Per cent. ester.....	37.1	33.2	30.2	26.7			
Temp.....	7.1	8.0	7.0	5.5			

(c) Solid Phase,  $CCl_3.COOH$ .

Per cent. ester.....	23.2	15.8	8.6	0
Temp.....	17.7	37.2	49.7	58.1

**14. Dimethyl Malonate.**—The ester was prepared in the usual manner, the product being finally fractionated *in vacuo*. The ester has not previously been frozen (m. p.  $-62^\circ$ ). Owing to supercooling with formation of glasses, mixtures containing between 60% and 100% of ester could not be examined. (The probable form of the curve is indicated by a broken line in Curve I, Fig. 2.)

A compound crystallizing in plates was isolated. It is unstable at its maximum but obviously, from the form of the curve near the break, is the compound  $CH_2(COO.CH_3)_2, 2CCl_3.COOH$  (compare Systems 12 and 13); m. p.  $-28.5$  (by extrapolation).

(a) Solid Phase,  $CH_2(COO.CH_3)_2$ .

Per cent. ester.....	100
Temp.....	$-62.0$

(b) Solid Phase,  $CH_2(COO.CH_3)_2, CCl_3.COOH$ .

Per cent. ester.....	60.9	54.4	50.0	45.8	41.7	37.8
Temp.....	-60.0	-46.1	-39.0	-34.0	-31.0	-29.2

(c) Solid Phase,  $CCl_3.COOH$ .

Per cent. ester.....	37.7	35.0	28.7	24.2	19.3	10.6	0
Temp.....	-28.7	-15.1	8.7	21.7	32.3	47.7	58.9

**15. Diethyl Oxalate.**—The m. p. of a Kahlbaum specimen was raised from  $-45^\circ$  to that given in the literature ( $-41^\circ$ ) by fractionation under diminished pressure. A compound just stable at its maximum was isolated, crystallizing in thin, seemingly triclinic plates (m. p.  $3.4^\circ$ ). (See Curve II, Fig. 2.)

(a) Solid Phase,  $(COO.C_2H_5)_2$ .

Per cent. ester	100	89.6	82.5
Temp.....	$-41.0$	$-43.5$	$-46.5$

(b) Solid Phase,  $(COO.C_2H_5)_2, 2CCl_3.COOH$ .

Per cent. ester	74.6	69.3	63.1	56.7	50.0	48.3	42.7	38.9	33.3	32.8
Temp.....	-46.5	-35.0	-23.6	-13.9	-5.9	-4.1	0.1	1.9	3.4	3.4

(c) Solid Phase,  $CCl_3.COOH$ 

Per cent. ester	35.9	30.8	23.9	17.0	8.7	0
Temp.....	-10.6	8.5	25.5	38.8	50.5	58.6

**16. Dimethyl Oxalate.**—A Kahlbaum specimen of satisfactory melting point was used. No compound could be isolated; on repeated trials mixtures around 50 mol per cent. always froze spontaneously to give characteristic plates of the ester. The form of the curve indicates, however, that much combination occurs in the liquid mixture.

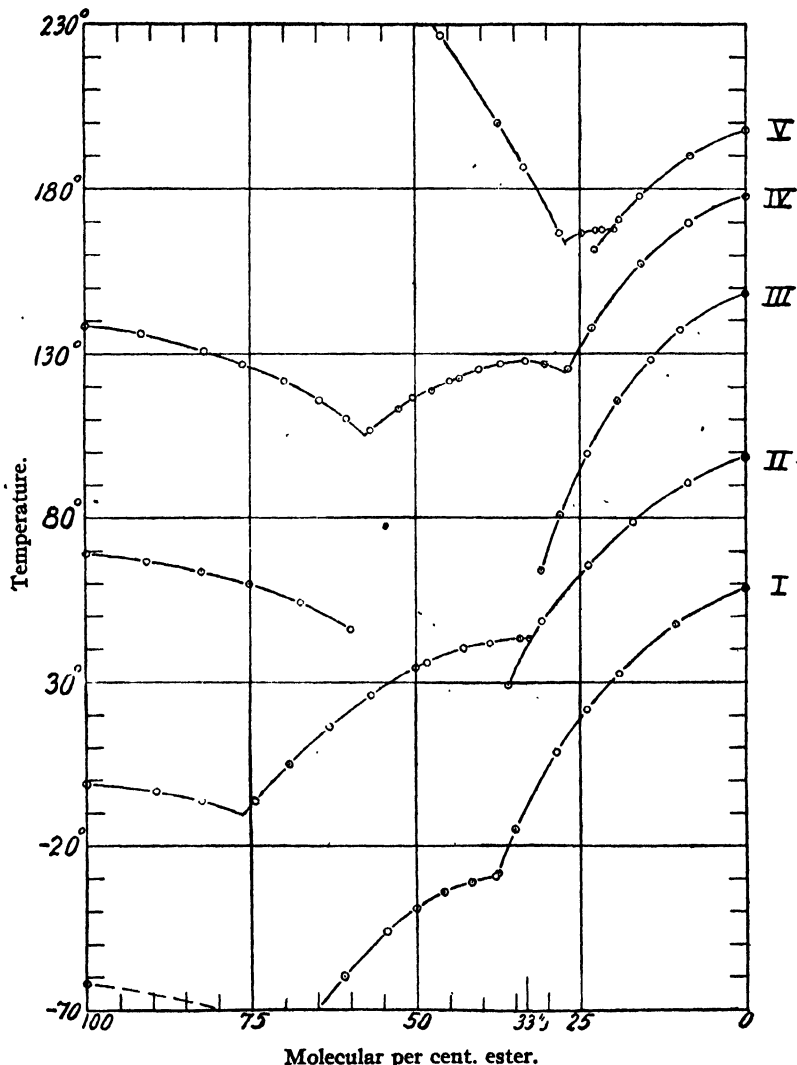
(a) Solid Phase,  $(\text{COO.CH}_3)_2$ .

Per cent. ester.....	100	91.3	80.6	72.9	63.6	56.7	50.0	45.3
Temp.....		53.3	49.4	42.9	36.4	28.4	20.0	10.3

(b) Solid Phase,  $\text{CCl}_3\text{COOH}$ .

Per cent. ester.....	40.0	33.8	26.9	17.2	8.3	0
Temp.....	2.5	15.5	27.5	41.6	50.9	57.9

Fig. 2.—Freezing-point curves of esters of dibasic acids with trichloroacetic acid.



- I. Dimethyl malonate (scale correct). IV. Dimethyl succinate (subtract  $120^\circ$ ).  
 II. Diethyl oxalate (subtract  $40^\circ$ ). V. Dimethyl terephthalate (subtract  $140^\circ$ ).  
 III. Diethyl succinate (subtract  $90^\circ$ ).

**17. Dimethyl Terephthalate.**—A pure specimen of the ester (m. p. 140.3) was furnished by Mr. C. P. Harris. This system is especially interesting, due to the fact that a compound,  $C_6H_4(COO.CH_3)_2,4CCl_3.COOH$ , was isolated. It would be expected by analogy to dimethyl malonate and succinate that only a compound  $AB_2$  should be formed. It is probable that a compound  $AB_2$  exists but its curve never enters the stable region.

As will be seen from Curve V, Fig. 2, the compound  $AB_4$  is only just stable at its maximum (m. p. 27.9°); it was consequently deemed advisable to analyze it. This was done by filtering and drying the large needles of the compound at a temperature of between 25° and 26°. The extremely hygroscopic crystals were weighed and added to water, whereby the compound was decomposed into its components. The acid was then titrated.

0.4563 g. crystals required 12.80 cc. 0.1683 normal NaOH. Found: 0.3520 g. trichloroacetic acid. Calc. for 1 : 4 compound: 0.3519 g.

(a) Solid Phase,  $C_6H_4(COO.CH_3)_2$ .

Per cent. ester.....	100	89.2	80.2	70.8	61.5	52.9	46.1	37.3	33.4	28.1
Temp.....	140.3	135.4	129.5	121.7	111.0	98.2	85.6	59.7	46.3	36.4

(b) Solid Phase,  $C_6H_4(COO.CH_3)_2,4CCl_3.COOH$ .

Per cent. ester.....	24.9	22.7	21.9	20.0
Temp.....	26.7	27.6	27.7	27.9

(c) Solid Phase,  $CCl_3.COOH$ .

Per cent. ester.....	22.7	20.0	19.2	15.9	8.3	0
Temp.....	21.5	28.2	30.4	37.9	50.1	57.8

**B. Systems with Chloroacetic and Acetic Acids.**—For curves see Fig. 4.

**18. Dimethyl Oxalate—Chloroacetic Acid.**—Both components, dried *in vacuo* over  $H_2SO_4$ , exhibited satisfactory melting points.

(a) Solid Phase,  $(COO.CH_3)_2$ .

Per cent. ester.....	100	89.3	76.5	71.0	64.3	57.2	50.1	49.3
Temp.....	53.2	49.3	44.7	41.0	37.3	32.6	27.6	27.0

(b) Solid Phase,  $CH_2Cl.COOH$ .

Per cent. ester.....	43.4	34.7	30.9	24.2	16.6	8.9	0.0
Temp.....	29.4	37.6	40.8	46.3	51.8	56.9	61.7

**19. Dimethyl Succinate—Chloroacetic Acid.**—

(a) Solid Phase,  $C_2H_4(COO.CH_3)_2$ .

Per cent. ester.....	100	90.3	81.0	71.4	62.4
Temp.....	18.2	14.8	10.8	5.9	0.1

(b) Solid Phase,  $CH_2Cl.COOH$ .

Per cent. ester.....	57.0	49.8	42.3	41.9	34.7	26.7	18.1	8.5	0.0
Temp.....	—3.5	7.4	18.0	18.5	28.1	38.0	47.4	56.2	61.9

**20. Methyl Cinnamate—Chloroacetic Acid.**—

(a) Solid Phase,  $C_6H_5.CH:CH.COO.CH_3$ .

Per cent. ester.....	100	84.8	77.2	73.4	63.9
Temp.....	34.4	27.4	23.4	20.0	14.5

(b) Solid Phase,  $\text{CH}_2\text{Cl.COOH}$ .

Per cent. ester.....	56.8	49.1	40.5	25.2	14.8	10.2	4.0	0.0
Temp.....	14.0	22.0	30.0	43.5	51.9	55.3	59.2	61.4

**21. Dimethyl Oxalate-Acetic Acid.**—A fractionation of 500 cc. of "glacial" acetic acid gave 65 cc. boiling between  $118-119^\circ$ , showing a m. p. of  $16.4^\circ$  and therefore 99.9% pure. Distillation from conc.  $\text{H}_2\text{SO}_4$  failed to give a good product.

(a) Solid Phase,  $(\text{COO.CH}_3)_2$ .

Per cent. ester.....	100	90.4	80.5	70.7	60.8			
Temp.....	53.2	50.3	47.5	44.5	41.3			
Per cent. ester.....	51.4	41.8	38.1	34.7	28.5	18.8		
Temp.....	37.3	32.5	30.5	28.2	23.8	14.1		

(b) Solid Phase,  $\text{CH}_3\text{COOH}$ .

Per cent. ester.....	9.9	0.0						
Temp.....	10.6	16.4						

**22. Dimethyl Succinate-Acetic Acid.**—(a) Solid Phase,  $\text{C}_2\text{H}_4(\text{COO.CH}_3)_2$ .

Per cent. ester.....	100	90.1	79.3	69.3	60.5	52.3	42.6
Temp.....	18.2	15.5	12.4	9.3	6.2	2.5	-2.2

(b) Solid Phase,  $\text{CH}_3\text{COOH}$ .

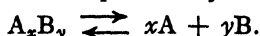
Per cent. ester.....	32.7	22.9	17.7	6.1	0.0		
Temp.....	-5.3	1.4	5.2	12.7	16.4		

From the preceding data it will be seen that, in each of the thirteen compounds isolated, trichloroacetic acid was the acid component. In no case did the weaker chloroacetic and acetic acids combine with the ester to a sufficient extent to allow a compound to be isolated. Likewise, the esters *not* yielding compounds with trichloroacetic acid are those of strong acids (dimethyl oxalate) or phenyl esters of moderately strong acids (phenyl benzoate and salicylate).

**5. Relative Stability of Addition Compounds.**

With regard to the relative stability of the oxonium salts obtained (*i. e.*, the extent of the combination of ester and acid in the liquid phase, as discussed on p. 1718), two lines of evidence may be brought forward.

(a) **Sharpness of Maxima.**—The addition compounds isolated are all more or less dissociated into their components in the liquid state. Their stability may be approximately determined from the sharpness of the maximum,<sup>1</sup> *i. e.*, the decrease in the temperature of fusion of the compound on addition of either component. The less the depression, or the flatter the curve in the neighborhood of the maximum, the greater is the dissociation at the melting point as expressed by the equation



In the following table some freezing-point lowerings for the compounds of trichloroacetic acid with esters are compared.

<sup>1</sup> Kendall, *Loc. cit.* See also Kremann, *Monatshefte*, 25, 1215 (1904).



TABLE II.—FREEZING-POINT DEPRESSIONS OF COMPOUNDS OF TRICHLOROACETIC ACID WITH ESTERS ON ADDITION OF EITHER COMPONENT.

System and type of compound. (A = ester. B = acid.)			Depression of freezing point ( $\Delta T$ ).	
			(a) 5 mol % from maximum.	(b) 10 mol % from maximum.
1. Ethyl acetate	AB.....	—27.5°	1.5°	5.2° <sup>2</sup>
2. $\alpha$ -Naphthyl acetate	AB.....	10.7	0.9	2.8 <sup>2</sup>
3. $\beta$ -Naphthyl acetate	AB.....	66.3	0.8	2.7
4. Ethyl benzoate	AB.....	—23.4	1.2	4.4 <sup>2</sup>
5. Methyl benzoate	AB.....	—8.8	1.1	4.2 <sup>2</sup>
6. Benzyl benzoate	AB.....	11.9	0.9	2.7
7. Methyl anisate	AB.....	—6.3	0.9	3.5 <sup>2</sup>
8. Methyl cinnamate	AB.....	8.5	1.5	5.3
9. Methyl <i>p</i> -toluate	AB.....	9.0	1.1	4.1
13. Dimethyl succinate	AB <sub>2</sub> .....	8.0	1.6 <sup>2</sup>	4.8 <sup>2</sup>
14. Dimethyl malonate	AB <sub>2</sub> .....	—28.2 <sup>3</sup>	1.02 <sup>2,3</sup>	4.02 <sup>2,3</sup>
15. Diethyl oxalate	AB <sub>2</sub> .....	3.4	1.2 <sup>2</sup>	3.8 <sup>2</sup>

For esters of monobasic acids (1 to 9), Column 4 gives the mean depression resulting from the addition of sufficient ester or acid to give a mixture containing, respectively, 55 or 45 molar per cent. of ester. Similarly, Column 5 gives the mean depression for mixtures containing 60 and 40 molar per cent. ester. For esters of dibasic acids (13–15) 61<sup>2</sup>/<sub>3</sub> and 56<sup>2</sup>/<sub>3</sub> molar per cent. of ester are chosen.

This method gives only an *approximate* indication of the relative stability of compounds of different esters with trichloroacetic acid. First of all the comparisons are not made at the same temperature, and secondly, the heat of fusion of the complex, related as it is to the freezing-point lowering, ought to be taken into consideration. Nevertheless, that the method is of value in affording qualitative relationships is evident from the following examples.

A sharper maximum, indicating greater stability, is obtained with the ethyl acetate compound than with the  $\alpha$ - or  $\beta$ -naphthyl acetates. So also is the depression somewhat greater for ethyl than for methyl benzoate and for these in turn markedly greater than in the case of benzyl benzoate. When we compare the methyl esters, the order of stability of the compounds becomes methyl cinnamate > methyl benzoate (or *p*-tolu-

<sup>1</sup> There is but little regularity in the melting points of the compounds isolated. They fall below or between those of the components. McIntosh's rule that the melting point of an oxonium compound is above that of either component is not general, but holds only for compounds with the low-melting hydrogen halides. In some cases the rule fails even here, as with C<sub>6</sub>H<sub>7</sub>OH, 2 HBr and C<sub>6</sub>H<sub>7</sub>OH, 5HCl, which melt lower than the respective hydrogen halides. (Archibald and McIntosh, *J. Chem. Soc.*, **85**, 928 (1904).)

<sup>2</sup> Depression caused by one component only.

<sup>3</sup> Obtained by a short extrapolation. Results are not included where extrapolation would be too great for accuracy.

ate) $>$ methyl anisate.<sup>1</sup> Likewise ethyl acetate exhibits a sharper maximum than ethyl benzoate. These relations are all to be expected from the comparative dissociation constants of the acids (see p. 1718). It is apparent from the above examples that the stability of the complex is greater for esters of weaker acids and where R' is more "positive" (*i. e.*,  $\text{C}_2\text{H}_5 > \text{CH}_3 > \text{C}_6\text{H}_5, \text{CH}_2$ , etc.). For esters of the dibasic acids the same rule holds, as will also be more clearly indicated by Method B below.

The quantitative investigation of the degree of dissociation of these compounds into the components, acid + ester, will be given in a later contribution.

(b) **Relative Slope of Curves.**—Addition compounds may be formed in the liquid phase and yet not be induced to crystallize out, especially if the degree of dissociation into the components at the melting point is large. In such cases, however, the extent of compound formation can be deduced from the change in slope of the freezing-point curve of either component. This gives, indeed, a more *general* method of detecting compound formation<sup>2</sup> than the actual isolation of the products.

On addition of any second substance, B, to a pure substance, A, the resultant lowering of the freezing point of A depends upon the molar fraction of the solute, B, present. If no combination of B with A occurs, the depression of the freezing point is expressed by the equation<sup>3</sup>

$$-\log x = \frac{Q}{RT_0} \left( \frac{T_0}{T} - 1 \right)$$

(where  $x$  = mol. fraction of A in mixture;  $Q$  = mol. heat of fusion of A;  $T_0$  = temperature of fusion of A;  $T$  = temperature of fusion of mixture;  $R = 1.988$ ). The form of this curve varies greatly with the relative values of  $Q$  and  $T_0$ . For organic compounds, in general, the values of  $Q$  and  $T_0$  are such that the ideal curve is, for the greater part of its length, approximately a straight line.

If, however, the addition of a foreign substance, B, to A is accompanied by the formation of an addition compound, AB, then the freezing point of A will be abnormally lowered, since part of the original solvent has been replaced by the second foreign substance AB. The more stable the compound is, the greater will be the abnormal depression of the freezing point. Hence the deviations from the ideal curve when different substances are added to A indicate the relative extent of combination in each case.

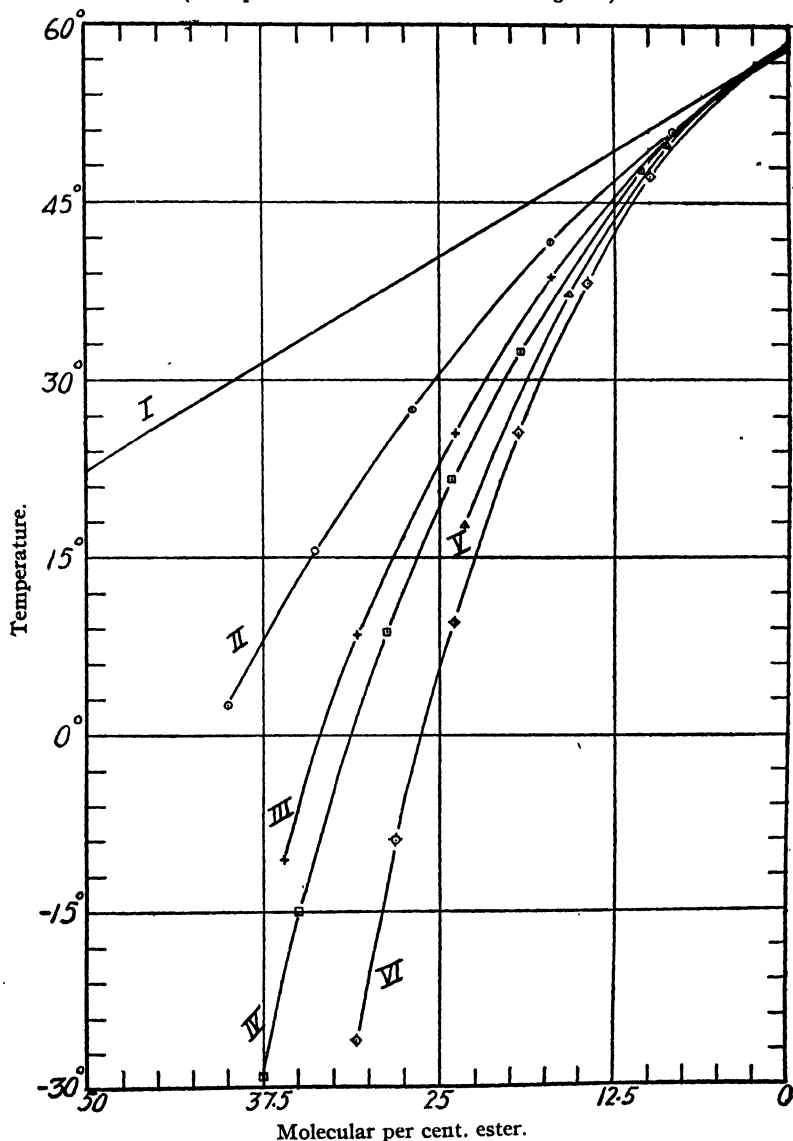
<sup>1</sup> Methyl anisate is an apparent exception to the general rule, as anisic acid being weaker than even cinnamic its ester should yield a compound *more* stable than that of the methyl cinnamate. That this is due to one of the factors making this but an approximate method is evidenced by the fact that methyl anisate shows a normal behavior by Method B, following.

<sup>2</sup> Kendall, *THIS JOURNAL*, 36, 1731 (1914).

<sup>3</sup> Roozeboom, *Heterogene Gleichgewichte*, 2, p. 273.

To establish the ideal curve for trichloroacetic acid it was examined with benzene, a substance with which it exhibits no compound formation. This is shown by the following table and more strikingly in Curve I, Fig. 3.

Fig. 3.—Freezing-point depressions of trichloroacetic acid with esters of dibasic acids (solid phase trichloroacetic acid throughout).



- I. Benzene.  
 II. Dimethyl oxalate.  
 III. Diethyl oxalate.

- IV. Dimethyl malonate.  
 V. Dimethyl succinate.  
 VI. Diethyl succinate.

## 23. Trichloroacetic Acid-Benzene.—

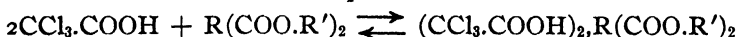
(a) Solid Phase,  $C_6H_6$ .

Per cent. $C_6H_6$ .....	100	89.6	84.3
Temp.....	5.4	1.5	—0.5

(b) Solid Phase,  $CCl_3.COOH$ .

Per cent. $C_6H_6$ .....	76.4	68.6	62.7	55.6	
Temp.....	—3.8	3.0	9.4	16.1	
Per cent. $C_6H_6$ .....	47.2	35.2	25.5	16.4	0
Temp.....	23.1	33.0	39.6	46.8	57.2

The comparison of this ideal freezing-point-depression curve for trichloroacetic acid with those caused by esters of various dibasic acids is shown in Fig. 3. Each of these esters lowers the temperature of fusion of trichloroacetic acid much more than does benzene, signifying extensive combination. If the reaction is represented as



each mol of ester on combination removes two mols of solvent. Consequently the dip of the curve is more decided than when an equimolecular compound is formed.

The "falling away" of the curve is greatest with diethyl succinate. The divergences assume the following order: diethyl succinate > dimethyl succinate > dimethyl malonate > diethyl oxalate > dimethyl oxalate. The following conclusions may be drawn: (1) Esters of the stronger acids combine less than esters of the weaker acids. (2) The diethyl ester of succinic or oxalic acid exhibits more combination than the corresponding dimethyl ester (the ether radical being somewhat more "positive" than the methyl radical).

The monobasic acid esters follow the same rules, confirming the results of Method A. This is shown in the table below, where freezing-point depressions of trichloroacetic acid due to 30 or 40 mol % of ester are compared.

TABLE III.—FREEZING-POINT DEPRESSIONS OF TRICHLOROACETIC ACID CAUSED BY ADDITION OF (a) 30 MOL %; (b) 40 MOL % OF AN ESTER.

Ester added.	(a) $T_0 - T_{\infty}$ .	(b) $T_0 - T_{\infty}$ .
1. Ethyl acetate.....	39.8°	78.8°
2. $\alpha$ -Naphthyl acetate.....	37.0	....
4. Ethyl benzoate.....	39.7	67.0
5. Methyl benzoate.....	38.5	63.5
6. Benzyl benzoate.....	36.3	60 $\pm$ 1° <sup>1</sup>
10. Phenyl benzoate.....	31.0	....
11. Phenyl salicylate.....	30.2	43.8
9. Methyl <i>p</i> -toluate.....	39.0	....
7. Methyl anisate.....	41.9	75 $\pm$ 2° <sup>1</sup>
8. Methyl cinnamate.....	38.8	....

As an example of the application of these data, the extent of compound

<sup>1</sup> Obtained by short extrapolation, the maximum uncertainty being indicated.

formation for the esters of benzoic acid is seen to be ethyl>methyl>benzyl>phenyl. Similarly methyl anisate manifests more combination than methyl cinnamate, benzoate, etc.<sup>1</sup> Other comparisons are readily made.

## 6. Compound Formation a General Phenomenon.

It has been established above that compound formation is general in systems containing trichloroacetic acid as acid component even in cases where no compound can actually be isolated. The same method may be employed to test the extent of compound formation in the similar systems (Nos. 18 to 22 above) containing weaker acids. We have here a means for determining the effect of variation of the third radical, X. At the same time we may compare the ideal curves for chloroacetic and acetic acids with those obtained on addition of different esters, and discover whether in these cases also general compound formation is indicated.

The normal curves for chloroacetic and acetic acids are established in the following tables:

### 24. Chloroacetic Acid-Benzene.—

(a) Solid Phase,  $C_6H_6$ .

Per cent. $C_6H_6$ ....	100	98.3
Temp.....	5.4	4.8

(b) Solid Phase,  $CH_2Cl.COOH$ .

Per cent. $C_6H_6$ ....	95.0	91.4	89.0	80.6	75.7	70.0	64.4	57.4	47.0	39.4
Temp.....	3.8	10.8	15.9	27.6	31.3	34.7	37.5	40.2	44.1	46.5
Per cent. $C_6H_6$ ....	30.9	24.9	18.3	8.7	0					
Temp.....	49.7	52.0	54.2	57.8	61.4					

### 25. Acetic Acid-Benzene.<sup>2</sup>—

(a) Solid Phase,  $C_6H_6$ .

Per cent. $C_6H_6$ ...	100	84.6	75.5	64.9	58.6
Temp.....	5.5	0.6	-2.4	-6.0	-8.4

(b) Solid Phase,  $CH_3.COOH$ .

Per cent. $C_6H_6$ ...	54.0	49.7	39.6	29.9	21.4	11.0	3.1	0
Temp.....	-7.4	-6.0	-1.8	2.3	6.0	10.7	14.0	16.3

These ideal freezing-point curves are compared in Table IV with those given for the same acids by dimethyl oxalate and dimethyl succinate, representing esters of strong and weak acids, respectively. The corresponding data for trichloroacetic acid are added for comparison.

TABLE IV.—COMPARATIVE FREEZING-POINT DEPRESSIONS OF ACIDS.

Solvent.	$\Delta T$ with dimethyl succinate.		$\Delta T$ with dimethyl oxalate.		$\Delta T$ with benzene.	
	25 mol %.	50 mol %.	25 mol %.	50 mol %.	25 mol %.	50 mol %.
$CCl_3.COOH$ ...	46.9°	...	27.4°	...	16.5°	36.2°
$CH_2Cl.COOH$ ..	21.9°	54.7°	15.5°	39.4° <sup>3</sup>	9.4°	18.4°
$CH_3.COOH$ ....	16.3°	...	13 $\pm$ 1° <sup>3</sup>	...	11.8°	22.3°

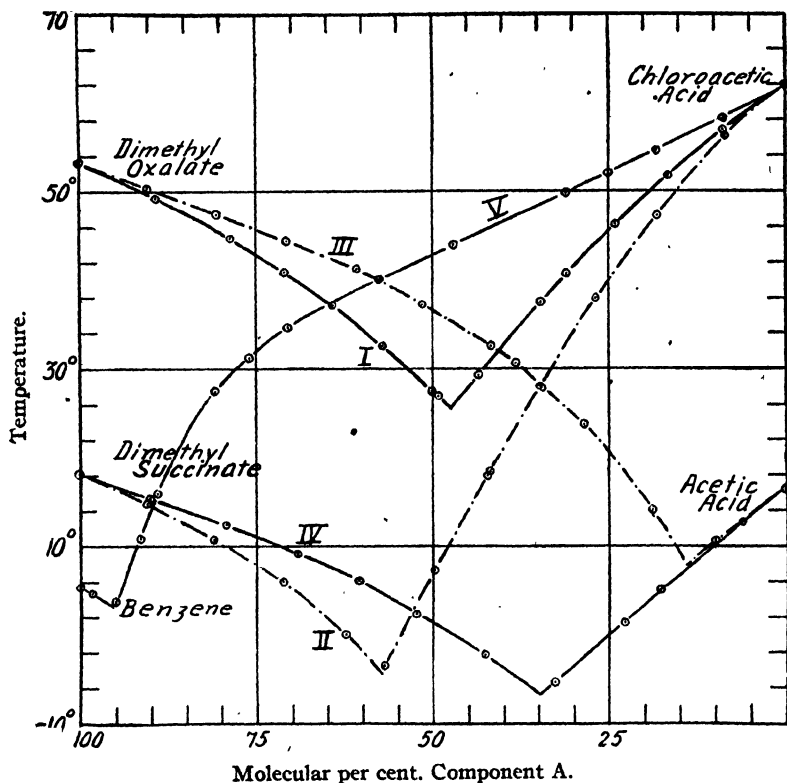
<sup>1</sup> See note 1, page 1730; methyl anisate here assumes its correct position.

<sup>2</sup> Data are those given by Roloff, *Z. physik. Chem.*, 17, 335 (1895); recalculated to molar concentrations.

<sup>3</sup> Values obtained by short extrapolation.

The observed freezing-point lowerings of chloroacetic and acetic acids by the three solutes selected are also shown graphically in Fig. 4. If we compare Curves I, II and V it is evident that benzene gives a normal curve throughout; both esters plainly cause abnormal depression. As before, combination is more extensive with the succinate than with the oxalate. The extent of compound formation with chloroacetic acid is, however, in both cases much less than with the strong acid, trichloroacetic.<sup>1</sup>

Fig. 4.—Freezing-point curves of chloroacetic and acetic acids with esters (solid phase for each curve is indicated at side of diagram).



- I. Dimethyl oxalate—chloroacetic acid.    IV. Dimethyl succinate—acetic acid.  
 II. Dimethyl succinate—chloroacetic acid.    V. Benzene—chloroacetic acid.  
 III. Dimethyl oxalate—acetic acid.

The acetic acid curves are less satisfactorily compared, as the break (change in solid phase) is too near the acetic acid axis. However, Table IV shows that the freezing-point depressions due to 25 mol per cent. of solute assume the same order as with other acids: dimethyl succinate > dimethyl oxalate > benzene. Similarly, from the other (left hand) branch

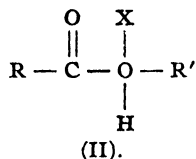
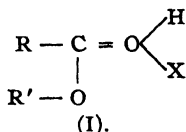
<sup>1</sup> See Figs. 2 and 3.

of the curves we see that the lowering of the temperature of fusion of dimethyl succinate by acetic acid deviates from the normal "straight line" curve<sup>1</sup> throughout; with dimethyl oxalate a slight "dip" in the curve becomes perceptible only when excess of acetic acid has been added. It is evident, therefore, that even the weak acetic acid combines to some extent with esters. The deviations from the normal curve vary, as before, with the ester considered, but some compound formation is indicated even in such an unfavorable system as acetic acid-dimethyl oxalate.

All acids catalyze ester hydrolysis, the degree of acceleration (for ordinary concentrations) increasing with the strength of the acid. When this is correlated with the fact that all acids form addition compounds with esters, the extent of compound formation also increasing with the strength of the acid, we are led to conclude that the formation of these addition compounds constitutes in reality the first step in ester hydrolysis. Further evidence on this point will be adduced in a subsequent communication.

### 7. Structure of Addition Compounds Isolated.

In these oxonium compounds, either the carbonyl or the hydroxyl oxygen may be quadrivalent, as is shown in Formulas I and II, respectively:



Kendall and Gibbons<sup>1</sup> and Kendall and Carpenter<sup>2</sup> have isolated many compounds of Type I and proved their structure; likewise compounds of alcohols and phenols with acids, illustrating Type II, have been investigated by McIntosh<sup>3</sup> and by Kendall.<sup>4</sup> The definite choice between the two formulas cannot yet be made.<sup>5</sup> It seems that the dimethyl terephthalate compound AB<sub>4</sub> may be a combination of both types.

It is at present premature to attempt to discuss the whole mechanism of ester hydrolysis, *i. e.*, how the oxonium compound, or its positive ion, finally suffers hydrolysis. Several such formulations of the hydrolysis have been put forth, with little experimental support. The authors are now endeavoring to obtain direct experimental evidence on the course of the reaction after the first step, formation of the binary oxonium compound.

<sup>1</sup> THIS JOURNAL, 37, 149 (1915).

<sup>2</sup> *Ibid.*, 36, 2498 (1914).

<sup>3</sup> J. Chem. Soc., 85, 928 (1904).

<sup>4</sup> THIS JOURNAL, 38, 1309 (1916).

<sup>5</sup> Compare Falk and Nelson, *Loc. cit.* Formula II is the one more favored by organic chemists, Stieglitz, Nelson and others having used it, without apparent justification beyond convenience of formulation.

### 8. Summary.

1. The formation of binary compounds of the type ester-acid has been investigated by the freezing-point method. Such compounds have heretofore been assumed to exist, to explain the mechanism of ester hydrolysis as catalyzed by acids, but no conclusive evidence of their presence has been produced. In the present investigation thirteen oxonium compounds of widely differing esters with trichloroacetic acid have been isolated, esters of monobasic acids uniformly yielding equimolecular compounds.

2. Previous papers indicated that oxonium compound formation is in general more evident the more divergent the "acidic strength" of the components employed.<sup>1</sup> Applied to the present case this would demand that combination be most pronounced between *strong* acids and esters of *weak* acids (preferably the alkyl rather than the more "negative" aryl esters). All *three* radicals concerned were varied experimentally as widely as possible and the rule was found to hold throughout the whole range of systems examined.

3. The extent of compound formation varies within wide limits as the above factors are varied. Although decreasing rapidly with decrease in strength of the acid it is still perceptible even with the typical weak acid, acetic acid. We may, therefore, state definitely that *oxonium salt formation is a general phenomenon in systems ester-acid*. These experimental results are in significant agreement with the fact that acceleration of ester hydrolysis is a general property of acids and also decreases with decrease in strength of the acid.

4. The results obtained in this paper are in entire agreement with the "intermediate compound formation" theory as an explanation of acid catalysis of ester hydrolysis. The formation of addition compounds of the type ester-acid as the first step in the mechanism of the reaction may now be regarded as experimentally established.

NICHOLS LABORATORIES OF INORGANIC CHEMISTRY,  
COLUMBIA UNIVERSITY, NEW YORK CITY.

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

## THE THERMAL DECOMPOSITION OF SYMMETRICAL DIARYL-HYDRAZINES.<sup>2</sup>

BY JULIUS STIEGLITZ AND HELEN TREDWAY GRAHAM.<sup>3</sup>

Received June 28, 1916.

In the thermal decomposition of hydrazobenzene, azobenzene and aniline are formed according to the equation



<sup>1</sup> Kendall and Gibbons, *THIS JOURNAL*, 37, 149 (1915).

<sup>2</sup> After the completion of the work reported in this paper and after the original



As shown in previous papers<sup>4</sup> from this laboratory, there are several possible courses which the reaction might take to give these products, the study of which seemed to us of special interest from the point of view of the theory of organic chemistry. One of these involves a preliminary dissociation of the hydrazobenzene into phenyl imide and aniline, the azobenzene being the product of a secondary polymerization of the phenyl imide:<sup>5</sup> writing of the same, a report by Wieland on the same subject (*Ber.*, 48, 1098 (1915)) came to hand, in which Wieland arrived at the same conclusion as we had, namely, that one must abandon for symmetrical diaryl hydrazines the theory of Stieglitz and Curme (*Ber.*, 46, 911 (1913)) and *THIS JOURNAL*, 35, 1143 (1913)), which ascribed the monomolecular character of the decomposition of hydrazobenzenes into aryl amines and azobenzenes, involving two molecules of hydrazobenzene, to a measurably slow decomposition of the hydrazobenzene into aryl imide  $\text{PhN} <$  and amine, followed by the fast polymerization of aryl imide to azobenzene. The monomolecular character of the reaction, discovered by Stieglitz and Curme, is not called into question. We should like to point out here that Dr. Curme, in his paper (*THIS JOURNAL*, 35, 1152, footnote 3 (1912)), stated that the critical experiment of the identification of the three possible azo compounds, which the theory would demand for the decomposition of hydrazines  $(\text{Aryl})\text{HN.NH}(\text{Aryl})$  would be made as soon as time permitted. As Dr. Curme left for Europe at that time, the work was continued from this point by Miss Tredway the same autumn and, working with methylhydrazobenzene, we found already, Nov. 10 and Dec. 8, 1913, and with bromohydrazobenzene on Jan. 10, 1914, that only one azobenzene is formed in each case—a result recognized at once as incompatible with the theory of Stieglitz and Curme. In consideration of Curme's reservation, we thought it best to make a much more elaborate investigation of the reaction, with a view to securing results for a positive basis of a revised theory before publishing our findings. We recognize now that an immediate preliminary publication would have been wiser; but we are glad to welcome the fact that in a large measure we are now in essential agreement with the findings of our brilliant German colleague. However, while not denying the possibility of Wieland's new hypothesis (his original one (*Ann.*, 392, 133 (1912)) was disposed of by the discovery by Stieglitz and Curme of the monomolecular character of the reaction), we have developed an alternative hypothesis which we consider of special significance and worthy of more extended investigation, because the reaction under discussion is only a typical case of that large and well-known class of reactions, in which products of an intermediate stage of oxidation are converted under the influence of heat into mixtures of products of lower and higher stages of oxidation. The hypothesis may also be extended to all kinds of oxidation-reduction reactions. In conclusion, we are glad to welcome the fact that Wieland and Reverdy (*Loc. cit.*, p. 1112), by substituting triphenylhydrazine for hydrazobenzene, have actually realized experimentally a thermal decomposition proceeding exactly along the lines of the theory of Stieglitz and Curme, to wit:  $(\text{C}_6\text{H}_5)_2\text{N.NH}(\text{C}_6\text{H}_5) \longrightarrow \text{C}_6\text{H}_5\text{N} + (\text{C}_6\text{H}_5)_2\text{NH}$  (a slow reaction) and  $2\text{C}_6\text{H}_5\text{N} \longrightarrow \text{C}_6\text{H}_5\text{N} : \text{NC}_6\text{H}_5$  (a fast reaction)—showing that the fundamental assumptions of the theory of Stieglitz and Curme were and are essentially sound, in spite of the fact that the dissociation of hydrazobenzene itself follows another course.—J. STIEGLITZ.

<sup>3</sup> The work presented in this article formed the basis of a dissertation submitted by Miss Tredway to the University of Chicago in August, 1915, in part fulfilment of the requirements for the degree of Doctor of Philosophy.

<sup>4</sup> Stieglitz and Curme, *Ber.*, 46, 911 (1913); Curme, *THIS JOURNAL*, 35, 1143 (1913).

<sup>5</sup> See Curme, *Loc. cit.*, in regard to an analogous dissociation into phenyl amide,  $\text{C}_6\text{H}_5\text{NH}$ .



Similar dissociation into unsaturated, reactive radicals had been quite commonly assumed in organic chemistry; the reaction in question seemed to be available for a particularly simple and decisive experimental test of the question by determination of the velocity of the decomposition reaction at a given temperature. A reaction proceeding according to Equations 2 and 3 would be a reaction of the *first order* for the measurably slow reaction (2), the union of phenyl imide radicals according to (3) following with a presumably far greater speed. In such a case, the velocity of the action at a constant temperature should satisfy the equations

$$\frac{dx}{dt} = K_{\text{mono}} (a - x) \quad (4)$$

and

$$K_{\text{mono}} = \frac{1}{t_2 - t_1} \ln \frac{a - x_1}{a - x_2} \quad (5)$$

The symbols have their usual significance.

On the other hand, if the reaction were one of intermolecular oxidation and reduction as expressed in Equation 1, and were due to the high reducing tension of the hydrogen attached to the nitrogen in hydrazobenzene,<sup>1</sup> we would have at a constant temperature a reaction of the *second order*, taking place with a velocity

$$\frac{dx}{dt} = K_{\text{di}} (a - x)^2, \quad (6)$$

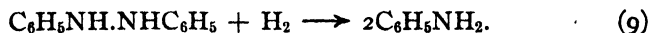
from which we find

$$K_{\text{di}} = \frac{1}{t_2 - t_1} \cdot \frac{x_2 - x_1}{(a - x_2)(a - x_1)} \quad (7)$$

In the first paper on this problem, the question was considered whether such an intermolecular oxidation and reduction could not also be a reaction of the first order, involving a preliminary dissociation of hydrazobenzene into azobenzene and hydrogen



followed by the reduction

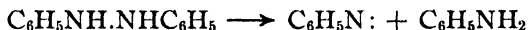


Inasmuch as the hydrogen had to have a very high reducing tension, and since it could not be considered to have this when it was once liberated as free hydrogen—which does not reduce hydrazobenzene—it was concluded that it could have this high reducing tension only while it was in unstable union with the nitrogen of the hydroazobenzene. Consequently it could be effective only when a second molecule of hydrazo-

<sup>1</sup> Wieland, *Ann.*, 392, 133 (1912); cf. Stieglitz and Curme, *Loc. cit.*

benzene actually met or collided with the first molecule. That would involve dynamically a true bimolecular reaction proceeding according to Equations 6 and 7.

The measurements of the velocities of the decomposition of hydrazobenzene, *p*-methylhydrazobenzene and *p*-hydrazotoluene by Curme showed unquestionably that the velocities followed the monomolecular law expressed in Equations 4 and 5: although some falling off of the constant was observed in the course of the decomposition of 75% of the substance in a given experiment,<sup>1</sup> the *initial velocities* in a range of concentrations from 0.054 to 0.22 molar, were uniformly the same<sup>2</sup>—a relation which, according to the best authorities, is a critical test for the order of a reaction. Furthermore, calculations of  $K_{di}$  according to Equation 7 showed a very wide variation during the course of a single determination, and an enormous variation with a change of the initial concentration.<sup>3</sup> Calculations likewise made very improbable the occurrence of parallel mono- and bimolecular decomposition reactions. The conclusion was therefore drawn that the thermal decomposition of hydrazobenzene is a reaction of the first order, and it was thought that the occurrence of an intermediate dissociation of hydrazobenzene, for instance, into phenyl imide and aniline according to



had been demonstrated. This was the main question the investigation was intended to settle.

Wieland,<sup>4</sup> in discussing these results, proposed the explanation, that the reaction measured was the slow decomposition of the hydrazine into azobenzene and *atomic* hydrogen and that this was followed by the immeasurably fast reduction of another molecule of hydrazobenzene by the liberated hydrogen. One of us had already considered the alternative possibility,<sup>5</sup> as shown above, that azobenzene and *ordinary* hydrogen are formed in a slow reaction and could not reconcile the assumption with the known facts: (1) that hydrogen does not appear to reduce hydrazobenzene under the conditions of the experiment, let alone reduce it with immeasurable speed; and (2) that no indications of the presence of free hydrogen were ever observed in Curme's experiments, carried out in sealed tubes. Both of these facts, it may be remarked here, were confirmed by careful experiments made in the course of the present investigation.

The problem at issue seemed settled therefore in favor of the disso-

<sup>1</sup> For instance, in 0.2 molal solution of hydrazobenzene, at 140.55°,  $10^5 \times K_{mono} = 157, 159, 159, 156, 153, 149, 144$ .

<sup>2</sup> Curme, *Loc. cit.*, tables, pp. 1158-9.

<sup>3</sup> For the 0.2 molal solution,  $10^4 \times K_{di} = 86$ ; and for 0.05,  $10^4 \times K_{di} = 370$ .

<sup>4</sup> *Die Hydrazine*, p. 51 (1913).

<sup>5</sup> Stieglitz and Curme, *Ber.*, 46, 914 (1913).

ciation theory (Equations 2 and 3), by the unquestioned order (monomolecular) of the reaction and by the experimental fact that a reduction of hydrazobenzene required a higher reducing tension than that possessed by free hydrogen.<sup>1</sup> But the whole problem was opened again for further investigation by the following observations: in the decomposition of hydrazines with two different aryl groups—such as *p*-methyl hydrazobenzene,  $C_6H_5NH.NHC_6H_4CH_3$ —a preliminary dissociation into phenyl imide radicals and anilines should yield ultimately three azo compounds,  $C_6H_5N : NC_6H_5$ ,  $C_6H_5N : NC_6H_4CH_3$  and  $CH_3C_6H_4N : NC_6H_4CH_3$ , and two anilines,  $CH_3C_6H_4NH_2$  and  $C_6H_5NH_2$ , presumably in unequal proportions, since the decompositions



and



would almost certainly not be equally favored. As a matter of fact, Dr. Curme's experimental data<sup>2</sup> showed that in the decomposition of *p*-methylhydrazobenzene, just about twice as much toluidine is formed as aniline. A reduction by way of Equations 8 and 9 would demand equal molar proportions of the two anilines. This result therefore agreed perfectly with the main conclusion drawn in favor of the dissociation theory. It was planned<sup>3</sup> to confirm the conclusion by identifying the three azo compounds which should be formed under these conditions, but Dr. Curme's departure for Europe necessitated the postponement of this examination. It was at this point that the present investigation was taken up, with the unexpected but convincing result that in the thermal decomposition of *p*-methyl-hydrazobenzene and of *p*-bromohydrazobenzene, only a *single azo compound* is produced—the one corresponding to the hydrazo compound used. Thus from methylhydrazobenzene,  $C_6H_5NH.NHC_6H_4CH_3$ , only methylazobenzene,  $C_6H_5N : NC_6H_4CH_3$ , is obtained; from *p*-bromohydrazobenzene,  $C_6H_5NH.NHC_6H_4Br$ , only bromoazobenzene,  $C_6H_5N : NC_6H_4Br$ , is produced.

This conclusion was amply confirmed by careful determinations of the proportions of anilines,  $C_6H_5NH_2$  and  $XC_6H_4NH_2$ , formed in the thermal decomposition: by the use of more elaborate and accurate methods than that used by Curme, it was found that the proportion is 1 : 1, as required for a direct reduction of a molecule of the hydrazobenzene,  $XC_6H_4NH.NHC_6H_5$ .

<sup>1</sup> Since then the actual existence and great reactivity of *atomic* hydrogen as compared with ordinary hydrogen has been demonstrated by Langmuir (THIS JOURNAL, 36, 1708 (1914) and 37, 417 (1915)).

<sup>2</sup> Curme, THIS JOURNAL, 35, 1171 (1913).

<sup>3</sup> Curme, *Loc. cit.*, p. 1152, footnote 3.

These results are irreconcilable<sup>1</sup> with the theory of a preliminary dissociation into phenyl imide radicals,<sup>2</sup> as expressed in Equations 3 and 4, and thus the whole problem of the mechanism of the reaction was reopened.

The following facts were next established:

(1) For concentrations ranging from 0.2 to 0.05 molar, the reaction is actually one of the first order, as found by Curme. The main experimental part of Curme's work was thus fully confirmed.

(2) In very dilute solutions (0.01 to 0.005 molar), the reaction is no longer clearly one of the first order; in individual experiments fairly good constants for a second order reaction (Equation 7) are obtained, but the constants for different concentrations do not agree at all with one another. The order of the reaction, therefore, in very dilute solutions is uncertain and probably neither wholly of the first nor of the second order.

(3) In a sealed tube charged with an alcoholic solution of an excess (relative to the hydrogen) of bromohydrazobenzene in an atmosphere of hydrogen, and heated for two hours at 145°, the temperature at which the decomposition reaction was studied, no absorption of hydrogen of any moment was discernible. There is, therefore, no direct reduction with immeasurable speed. The action



must therefore be considered excluded in the theory of the thermal decomposition of arylhydrazines.

(4) In extremely dilute solutions (0.01 molar), a little permanent gas is formed, but it fails to respond to the tests for hydrogen, made both with palladium and oxygen, and with oxygen in an explosion pipet<sup>3</sup> (see the experimental part). The absence of hydrogen, taken in conjunction with its failure to react when used with hydrazobenzene, shows that ordinary hydrogen cannot be considered an intermediate product in the thermal decomposition of the arylhydrazines.

(5) The molecular weight of *p*-bromohydrazobenzene was determined in boiling absolute alcohol solution and found to be that of the simple

<sup>1</sup> See Wieland, *Ber.*, 48, 1098 (1915) and the introductory note to this article.

<sup>2</sup> A dissociation of this type, however, was found by Wieland and Reverdy (*Ber.*, 48, 1112 (1915)) to occur in the case of triphenylhydrazine,  $(\text{C}_6\text{H}_5)_3\text{N.NHC}_6\text{H}_5$ .

<sup>3</sup> As the exact nature of this permanent gas, especially as to the question of its containing hydrogen, seemed of particular theoretical significance (see below), Mr. E. N. Roberts in the autumn of 1915 kindly undertook its re-examination. He confirmed the finding of Mrs. Graham that it contains no hydrogen and further established the fact that aside from the presence of the small amount of oxygen and nitrogen left as air in the tube sealed under 18 mm. pressure, a very large proportion of nitrogen is present (at least 75% of the total volume in excess of the air nitrogen). The nitrogen was converted into ammonia by sparking it with hydrogen over sulfuric acid, and the ammonia determined both by titration and by nesslerizing.—J. S.

molecule,  $\text{C}_6\text{H}_5\text{NH.NHC}_6\text{H}_4\text{Br}$ . The simple explanation<sup>1</sup> of a reaction of the first order between two molecules of hydrazobenzene as being due to a dimolecular form is thus excluded. The monomolecular form being found at  $78^\circ$ , there should be no polymerization at  $140^\circ$  and  $150^\circ$ , the temperatures at which the experiments were conducted. The possibility that in a reversible reaction



small quantities of a dimolecular form are present and decomposed, would clearly lead to "constants" varying with the concentration,<sup>2</sup> and this possibility is therefore also excluded.

We are thus called upon to reconcile the fact that the thermal decomposition of hydrazines in solutions of moderate concentration (0.05 to 0.2 molar) is certainly one of the first order indicating a decomposition of only a *single molecule*—with the fact that no ordinary decomposition product of the single molecule, namely neither phenyl imide,<sup>3</sup>  $\text{C}_6\text{H}_5\text{N}$ ·, nor hydrogen,  $\text{H}_2$ , can be formed as an intermediate product, and with the further fact that a *second* molecule of the hydrazobenzene is nevertheless reduced at great speed in some way as the result of the decomposition of the first molecule. We have, in a word, a dimolecular reaction of the first order. Two possible explanations of this set of facts suggest themselves as the most plausible ones. The first of these<sup>4</sup> is that the monomolecular reaction, whose velocity we have measured, is a decomposition of the hydrazobenzenes into azobenzene and *atomic* hydrogen. Langmuir<sup>5</sup> has recently proved that atomic hydrogen is capable of existence, and is *vastly more reactive* than ordinary or molecular hydrogen. The high reducing tension of the hydrogen which, as we have seen, is neces-

<sup>1</sup> This explanation was apparently not considered by Wieland.

<sup>2</sup> If  $C_{di}$  and  $C_{mon}$  represent the respective concentrations of the dimolecular and monomolecular forms at any moment of equilibrium, we have  $C_{di} = K_{eq} \times C_{mon}^2$ . For a reaction, which might be of the first order for the polymerized form,

$$\frac{dx}{dt} = K_{vel} \times C_{di}$$

we would have by substitution

$$\frac{dx}{dt} = K_{vel} \times K_{eq} \times C_{mon}^2.$$

Consequently, if the main amount of hydrazobenzene is present in the monomolecular form—as has been proved by our experimental work—the order of the reaction would still appear as of the second order, even if the small amounts of the dimolecular form were the reacting component. Only if  $K_{eq}$  were quite large and by far the greater part of the substance were present in the associated form, would the reaction appear as one of the first order, the dependence of the associated molecules on the nonassociated ones involving only a small error, which could be within the limits of the experimental error.

<sup>3</sup> Or phenyl amide,  $\text{C}_6\text{H}_5\text{NH—}$ .

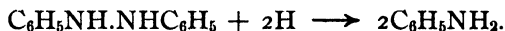
<sup>4</sup> Wieland, "Die Hydrazine," p. 51 (1913); and *Ber.*, 48, 1098 (1915).

<sup>5</sup> THIS JOURNAL, 36, 1708 (1914); 37, 417 (1915).

sary for the reduction of a second molecule of hydrazobenzene may reside and be maintained therefore not only in hydrazobenzene itself, but also in atomic hydrogen sufficiently long for the latter to reach and reduce the second molecule of hydrazobenzene. We would have,



and



This is an important modification of a possible monomolecular reaction given by Stieglitz and Curme in their first paper, in which the formation of ordinary hydrogen,  $\text{H}_2$ , was considered.<sup>1</sup> The present view was first advanced by Wieland.<sup>2</sup> It would overcome the objections to the original interpretation raised by Stieglitz and Curme—objections which without this modification would still exist. The modification consists in the assumption that the hydrogen is *atomic* hydrogen of a proved much higher degree of activity than that possessed by ordinary hydrogen.

Now, while we consider this explanation of the thermal decomposition of hydrazobenzenes a possible one, there are certain objections to it, which should be pointed out. In the first place, it should require *time* for the atomic hydrogen to *diffuse* through the solution to the second molecule of hydrazobenzene and reduce it; and instantaneous reduction is therefore out of the question. In the second place, in this process of diffusion, two separate atoms of hydrogen would have to move toward the same hydrazobenzene molecule—the *directing cause for which coincidence it would be hard to find*. And, finally, in this irregular diffusion it is certainly to be expected that a measurable part at least of the atomic hydrogen would, by a collision of the atoms, form ordinary *unreactive* hydrogen, especially in view of the original *proximity* of the two atoms, in leaving the mother hydrazone molecule, compared with the distance to a further molecule of hydrazine. As emphasized above, in solutions of moderate concentration no indications of the formation of any permanent gas at all were obtained; and in dilute solutions (0.01 molar), where a little permanent gas was obtained, it failed to respond to any test for hydrogen.<sup>3</sup> These considerations, and especially the last one, it seems to us, make the alternative hypothesis which we will now present, more likely to be the correct interpretation of the reaction.

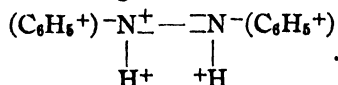
This interpretation, based on the electron theory of valence, has interested us in particular because one of us has long suspected the possibility of oxidation and reduction in solution occurring by a transfer of electrons from molecule to molecule, *without the necessity of a collision* (or approach to within molecular distances) *between the respective mole-*

<sup>1</sup> *Loc. cit.*

<sup>2</sup> *Die Hydrazine*, p. 51 (1913).

<sup>3</sup> See footnote 3, p. 1741.

rules. The present case is, we believe, the first instance where evidence of such an action has been recognized in solution in a simple thermal reaction.<sup>1</sup> According to the electron theory of valence, hydrazobenzene, in common with hydrazines in general, has the structure<sup>2</sup>



When it forms azobenzene and aniline, two electrons are discharged by the nitrogen of the one (reducing or oxidized) molecule, producing azobenzene,  $(\text{C}_6\text{H}_5^+) - \text{N}^+ = \text{N}^- (+\text{C}_6\text{H}_5)$  or  $(\text{C}_6\text{H}_5^+) - \text{N}^+ = \text{N}^- (+\text{C}_6\text{H}_5)$ , and releasing, as a consequence, two positively charged hydrogen atoms or ions. On the other hand, the nitrogen of the second (reduced) molecule absorbs two electrons to form aniline, in which the nitrogen is unquestionably wholly negative,<sup>3</sup>  $(\text{C}_6\text{H}_5^+) \text{N} \equiv (\text{H}^+)_3$ , as in ammonia; the absorption of two electrons must disrupt the union of the nitrogen atoms in this second molecule of hydrazobenzene, and give to the two negative radicals or ions  $\text{C}_6\text{H}_5\text{NH}^-$  formed the power to absorb two positively charged hydrogen atoms or ions (see the equations below). Now, it is easily conceivable that the two electrons discharged by the reducing (oxidized) molecule should pass with very great speed through the solution to the positive valence of the nitrogen in the second molecule; electrons have, of course, at a given temperature, normally, velocities perhaps forty times as great as hydrogen atoms, at the same temperature; and moreover, on account of their volume being, let us say, 1800 times as small as that of the hydrogen atom, they would meet with an enormously smaller resistance in a liquid medium than hydrogen atoms would. Electrons are known indeed to pass even through the interstices of atoms. The two electrons in question could therefore reach the second molecule of hydrazobenzene with a sufficient speed to be negligible; charging the nitrogen of this molecule wholly negatively, they would sunder the molecule, and the negative phenyl amide radicals would unite with two positive hydrogen atoms, derived either from the medium surrounding them or from the oxidized hydrazobenzene molecule. The *actual* reduction<sup>4</sup> would consist in the absorption of the two electrons—the union with the

<sup>1</sup> Bodenstein (*Z. physik Chem.*, 85, 330 (1913)) has treated photochemical effects from a similar point of view. The work of Lind (*J. Phys. Chem.*, 16, 494 (1912)) on the influence of radioactive rays on the oxidation of hydrogen by halogens and the work of H. S. Taylor (*THIS JOURNAL*, 37, 24 (1915)) are also suggestive in this connection. C. A. Kraus (*THIS JOURNAL*, 36, 864 (1914)) proved the independent existence of electrons in the colored solutions of the alkali metals in ammonia.

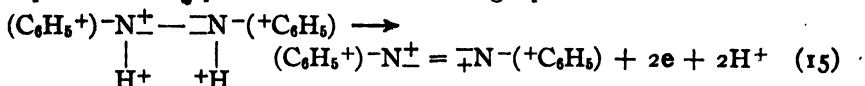
<sup>2</sup> Only the essential charges are indicated.

<sup>3</sup> In regard to its first three valences.

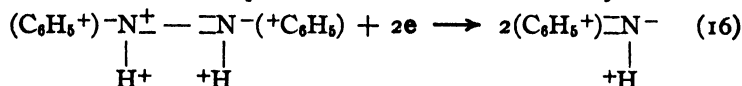
<sup>4</sup> A well-known conception. See, for instance, Stieglitz, "Qualitative Analysis," Vol. I, pp. 251-298 (1911).



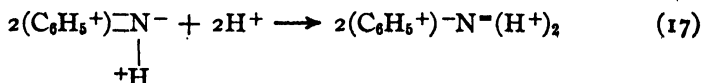
positive hydrogen is a simple ionic union of anions and cations. We can express this interpretation<sup>1</sup> in the following equations:



which would be a slow decomposition reaction, whose velocity is measured;



and



which would be exceedingly fast reactions, following the first slow decomposition reaction.

It should be observed that such an action would produce local potential differences in small elements of space; for instance, if  $\text{H}^+$  were liberated at the end of one such element and  $-\text{OC}_2\text{H}_5$  at the other end when  $\text{H}^+$ , derived from the solvent, is absorbed by the second molecule of hydrazobenzene, we would have for a small time interval, a local potential difference. The same situation would result if the positive hydrogen finally absorbed were the  $\text{H}^+$  given off by the first (oxidized) molecule of hydrazobenzene; since the electrons are considered to reach the second (reduced) hydrazobenzene molecule with far greater speed than the  $\text{H}^+$ , we would have local polarization in which in the small element of space, the hydrogen would be positive, the phenyl amide,  $\text{C}_6\text{H}_5\text{HN}^-$ , would be negative. Such potential differences would be distributed exceedingly irregularly, that is, in all directions, and would neutralize each other with greatest rapidity by irregularly distributed currents or combinations of ions in the elements of space. It is evident, further, that such a transfer of electrons would become much more difficult in solutions of extreme dilution,

<sup>1</sup> This electronic interpretation lends itself equally well to the decomposition of triphenylhydrazine into diphenylamine and azobenzene by way of an intermediate dissociation into diphenylamine and the phenyl imide radical  $\text{C}_6\text{H}_5\text{N}$ , as postulated by the theory of Stieglitz and Curme and realized by Wieland and Reverdy (*Loc. cit.*). In this case the primary action is one of *intramolecular* oxidation-reduction, instead of an intermolecular one as for hydrazobenzene.

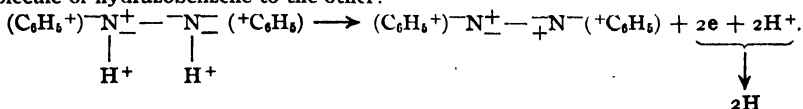


is the initial action, two electrons, designated by heavy type for the corresponding negative charges, passing from the phenyl amide nitrogen atom to the diphenylamide nitrogen atom to make the latter wholly negative. As a result, the union between the nitrogen atoms is rendered and  $\text{H}^+$  is also lost by the one nitrogen atom, and either transferred directly to the ion  $(\text{C}_6\text{H}_5)_2\text{N}^-$  or it takes the place of a hydrogen ion absorbed by the latter from the solution. The union of two phenylimide radicals to form azobenzene completes the action.

and that as a result the simple order of the action could be changed. This might account for the change in the order of the reaction, when we use very dilute solutions (0.01 molar), from a simple monomolecular one to an indefinite one. In particular, we would recall in this connection the fact that Bodenstein found that the combination of chlorine with hydrogen under the influence of alpha particles is *independent of the concentration of the reducing hydrogen down to a certain limiting concentration of hydrogen*. In the instance we are discussing, we may say that the velocity of the action seems to be independent of the concentration of the molecules of hydrazobenzene down to a certain limiting concentration—which makes the action essentially monomolecular down to that limit.

We recognize the hypothetical character of this theory,<sup>1</sup> but are proposing it not only as an attractive working hypothesis for the case under consideration, but as opening up a problem in the field of the dynamics of oxidation and reduction that has long interested one of us. The theory seems to us to have advantages over the first theory involving atomic hydrogen in that it gives a reasonable explanation of an almost instantaneous reduction of the second molecule of hydrazobenzene, unhampered by the necessity of instantaneous diffusion of such large atoms as hydrogen through an obstructing liquid, in that it gives a reasonable explana-

<sup>1</sup> The alternative hypothesis that *atomic* hydrogen is first released by the reducing molecule of hydrazobenzene (Wieland's later theory), when analyzed from the electronic point of view, simply signifies that the two electrons discharged by the nitrogen of this reducing molecule of hydrazobenzene are *first absorbed* by the two positive hydrogen atoms held by the nitrogen, instead of passing directly, as free electrons, from one molecule of hydrazobenzene to the other:



The two atoms of hydrogen would then pass through the solution (without any evident directive force) to the second molecule of hydrazobenzene and would there lose the two electrons to a nitrogen atom of the latter and be absorbed as positive hydrogen atoms. The difference between the two theories is then essentially the question whether we must assume the formation of an *intermediate product*, atomic hydrogen, as the *carrier of the electrons*, or whether we must assume the direct transfer of the electrons. Since the independent existence of electrons as atoms and molecules has been amply demonstrated, it seems to us the question raised is not only a reasonable one, but indeed one of fundamental interest. Further investigation of the actual relations seems, therefore, highly desirable; this will include among other methods of attack, attempts to detect any possible (perhaps momentary) conductivity in the solutions in which the decomposition is proceeding, as well as further investigation of the gas formed in extreme dilution. In conclusion, it should be said that this whole problem, *mutatis mutandis*, will be investigated in connection with other well-known cases of oxidation-reduction, especially also of compounds of an intermediate stage of oxidation, both in organic and especially also in well-known inorganic reactions.—J. S.

tion of the fact that no free hydrogen has been observed in the study of the decomposition; and in introducing a directive force (due to the positive charge on the nitrogen of the oxidizing molecule of hydrazobenzene) for the migration of two particles (electrons), to the same molecule.<sup>1</sup>

### Experimental Part.<sup>2</sup>

BY HELEN TREDWAY GRAHAM.

**1. Preparation and Analysis of the Hydrazo Compounds.**—The three hydrazo compounds used in this investigation—*p*-methylhydrazobenzene, *p*-bromohydrazobenzene, and 2,4-dichlorohydrazobenzene—were prepared by reduction of the corresponding azo compound with zinc dust in alkaline alcoholic solution. The azo compounds themselves were made by the method of Mills<sup>3</sup> from nitrosobenzene and the substituted aniline. The *p*-methylhydrazobenzene was identical in every respect with that described and used by Curme.<sup>4</sup> In preparing the halogen hydrazo compounds, a pink impurity was noticed, the nature of which was not investigated, but which could be removed only by several recrystallizations of the azo compounds before reduction.

***p*-Bromohydrazobenzene**,  $p\text{-BrC}_6\text{H}_4\text{NH.NHC}_6\text{H}_5$ , made by reduction of pure *p*-bromoazobenzene (m. p.  $89^\circ$ ), and twice recrystallized from alcohol containing a few grams of zinc dust and several drops of concentrated ammonium hydroxide solution, was obtained as shiny, white plates

<sup>1</sup> A third interpretation of this characteristic monomolecular oxidation and reduction reaction, involving ultimately two molecules of hydrazobenzene, is found in a combination of the two theories that have been presented. That is, the first, measurably slow reaction, may consist in the loss of two electrons by the reducing molecule of hydrazobenzene to a *single* one of the hydrogen atoms  $\text{H}^+$  which it loses—making it a *negative* hydrogen atom  $\text{H}^-$ , of even greater reducing power than atomic hydrogen. Negative hydrogen has been assumed by Fry (*Z. physik. Chem.*, **76**, 385 (1911) and later papers in *THIS JOURNAL*) to exist in certain organic compounds, and it certainly exists and shows its tremendous reducing power in the salts of hydrogen, such as sodium, potassium or calcium hydrides. The detailed application of the idea of the formation of negative hydrogen to the interpretation of the reaction we are investigating is not necessary, as it is indicated sufficiently clearly by our previous discussion. It would, it seems to us, have the advantage over Wieland's theory of the formation of atomic hydrogen, that we would have only a single atom of hydrogen moving to the second molecule of hydrazobenzene to reduce it, which would be guided moreover by the electrical attraction between its negative charge and the positive charge on the nitrogen. It should, however, lead still more easily and almost inevitably to the formation of some ordinary hydrogen  $\text{H}_2$  by collision with a hydrogen ion and for this reason we believe our theory of a direct transfer of electrons is most likely to be found to be the correct interpretation of the reaction.

<sup>2</sup> I take pleasure in using this opportunity of thanking my young collaborator, Mrs. Graham, to whose skill and perseverance the experimental part of this investigation is wholly due.—J. S.

<sup>3</sup> Mills, *J. Chem. Soc.*, **67**, 929 (1895).

<sup>4</sup> Curme, *Loc. cit.*, p. 1166.

melting at  $101-101.5^{\circ}$ .<sup>1</sup> Once dry, *p*-bromohydrazobenzene is very stable at ordinary temperatures; a sample was left exposed to the air of the laboratory for two weeks before it showed the slightest discoloration or change in melting point. For the determination of its purity the substance was oxidized in absolute alcohol with 0.1 *N* iodine solution. The solutions were made up and the analysis carried out exactly as described by Curme for hydrazobenzene,<sup>2</sup> except that we found it necessary to allow the iodine to act on the bromohydrazobenzene for an hour instead of ten minutes before acidifying the mixture and titrating the excess of iodine with thiosulfate. A weighed amount of 0.1 *N* iodine solution was first introduced into a glass-stoppered Erlenmeyer flask, and to it was added alcoholic aniline solution (approximately 0.1 *N*), sufficient to give an excess of 2-3 cc. over the amount required to neutralize the hydriodic acid to be formed in the subsequent oxidation. The weighed sample of *p*-bromohydrazobenzene was then dissolved in absolute alcohol and transferred with rinsing to the flask containing the iodine. The whole mixture was allowed to stand one hour, was then acidified with 10 cc. 6 *N*-sulfuric acid, and diluted to approximately 500 cc. with water. Bright yellow crystals of bromoazobenzene were thus precipitated. Standard 0.1 *N* thiosulfate solution was then run in until the fading of the brown color of the iodine indicated the approach of the end point, and starch indicator (10 cc.) was added, producing a greenish black discoloration. The thiosulfate solution was then introduced drop by drop until the bright yellow color of the azo compound was just restored. Blank experiments showed that the factor of the iodine solution was not materially affected by the presence of the aniline solution or by evaporation during the hour it was allowed to stand.

0.2901 and 0.2092 g. subst. required 15.24 and 15.92 g. 0.1 *N* iodine. Theory: 15.23 and 15.90 g.

**2,4-Dichloroazobenzene**,  $\text{Cl}_2\text{C}_6\text{H}_3\text{N}:\text{NC}_6\text{H}_5$ .—The preparation and purification of this substance offers much more difficulty than that of the other azo compounds employed. 2,4-Dichloroaniline was dissolved in glacial acetic acid, and nitrosobenzene added to the warm solution, which was refluxed for an hour. Cooling precipitated a black crystalline mass, which was collected on a filter, washed with 50% alcohol, dried thoroughly by suction, and extracted with ligroin (b. p.  $30-50^{\circ}$ ). The ligroin solution was filtered from black insoluble particles and evaporated to dry-

<sup>1</sup> Janovsky and Erb (*Ber.*, 20, 364 (1887)), who reduced *p*-bromoazobenzene with ammonium hydrosulfide in alcoholic solution, give the melting point of the hydrazo product as  $115^{\circ}$ ; this method of reduction was tried and gave a product with the melting point,  $101-101.5^{\circ}$ , given above. Janovsky and Erb also give an incorrect melting point,  $85^{\circ}$ , for *p*-bromoazobenzene (*Ber.*, 19, 2155 (1886)).

<sup>2</sup> *Loc. cit.*, p. 1155.

ness. The product was then recrystallized from 95% alcohol several times, until it had a constant melting point of  $105^{\circ}$ , and a brilliant orange color. The best yield of crude dichloroazobenzene obtained was 45%, and recrystallization to the required purity reduces the yield to 10–20%. Addition of water to the acetic acid solution filtered from the black mass, and to the wash liquid, precipitated fine light green needles which were very soluble in alcohol, melted at  $137^{\circ}$ , and on recrystallization from dilute alcohol, melted at  $139^{\circ}$ . Mixed with acetodichloroanilide (white rhombohedrous melting at  $143^{\circ}$ ), they melted at  $100^{\circ}$ , which proved that they were not acetodichloroanilide. No further attempt was made to determine the nature of the green product.

**2,4-Dichlorohydrazobenzene**,  $\text{Cl}_2\text{C}_6\text{H}_3\text{NH.NHC}_6\text{H}_5$ .—The azo compound can be reduced almost quantitatively to 2,4-dichlorohydrazobenzene by treatment with zinc dust in ammoniacal alcoholic solution, filtration from the zinc dust in an atmosphere of carbon dioxide, and precipitation of the hydrazo compound with warm, air-free water. The oil which first separates out, crystallizes on cooling. The product so obtained, even after several recrystallizations, invariably contained a trace of pink impurity similar to the one observed occasionally in the preparation of *p*-bromohydrazobenzene. As dichlorohydrazobenzene very easily becomes contaminated with some dichloroazobenzene by oxidation, material which was pinkish yellow in color, melted at  $73.5\text{--}74^{\circ}$ , and analyzed 95–96% pure, was used in the velocity experiments. A very small amount of pure dichlorohydrazobenzene was obtained by reduction of the purest dichloroazobenzene, the pink impurity being removed from the hydrazo compound by fractional precipitation with warm water. The slight amount of impurity present was entirely precipitated by a quantity of water insufficient to precipitate all the hydrazo compound; and as the solution was carefully protected from the air, the addition of more water to the filtrate precipitated almost colorless plates of dichlorohydrazobenzene, which melted at  $74.5^{\circ}$ , and analyzed 99.7% pure. Dichlorohydrazobenzene is so easily oxidized that it was found necessary to allow only ten minutes for the action of the iodine. In the analyses of this substance, no aniline was used to neutralize the hydriodic acid formed; but instead, the oxidation was carried out in the presence of sufficient acid ammonium carbonate to neutralize the acid formed in the oxidation, and in the presence of carbonic acid, liberated by the addition of acid ammonium carbonate to a measured quantity of hydrochloric acid. This method of neutralization was developed in connection with the work on the ratio of the two amines formed in the decomposition of *p*-bromohydrazobenzene and was found quite as satisfactory as the use of aniline.

0.1395 g. subst. required 10.99 g. 0.1 *N* iodine. Calculated, 11.02 g.

**2. Thermal Decomposition Products of Asymmetrical Hydrazobenzenes.**<sup>1</sup>—In order to find out whether a mixture of azobenzene and its mono- and di-substituted derivatives could be separated into its components on the basis of their different solubilities in alcohol, 0.5 g. azobenzene, 0.5 g. *p*-methylazobenzene, and 0.5 g. *p*-azotoluene were thoroughly powdered and mixed, and the mixture extracted with 15 cc. 95% alcohol at 0°. The yellow crystals obtained by the evaporation of the alcohol melted at 46–47°, while the part which did not dissolve in the alcohol melted at 59–61°. A second extraction with 10 cc. alcohol at 0° left a residue which melted at 117–137°, while evaporation of the alcohol yielded crystals melting at 47–48°. The melting points of azobenzene, *p*-methylazobenzene, and *p*-azotoluene are 69°, 70° and 144°, respectively. It is therefore clear that, even without completing the separation, fractionation with alcohol at 0° would very easily distinguish between a mixture of the three azo compounds and *p*-methylazobenzene alone.

*p*-Methylhydrazobenzene (1.7 g. in 10 cc. absolute alcohol) was then heated for fifteen hours at 125°, in tubes which had been sealed off at a pressure of 15 mm. The solution was allowed to evaporate in the air, after dilute hydrochloric acid had been added to acid reaction with litmus, for the purpose of neutralizing the amines formed by the decomposition. Orange-colored crystals appeared, which were transferred to a filter with water, and washed with water till they were free from acid. When dry, they melted at 70°. They were extracted three times with 10 cc. alcohol at 0°, and the residues and the crystals from evaporation of the alcohol melted uniformly at 70°, alone and when mixed with a known sample of *p*-methylazobenzene. An independent experiment showed that under the conditions used, *p*-azotoluene would not have been acted upon by the aniline present, the reaction



being thus excluded. Therefore, no *p*-azotoluene was formed in the decomposition of *p*-methylhydrazobenzene.<sup>2</sup> Exactly the same results were obtained when the products of the decomposition in 0.2 molal solution were examined.

The experiment was then repeated with 2.8 g. *p*-bromohydrazobenzene in 10 cc. absolute alcohol and perfectly analogous results were obtained.<sup>3</sup> Fractionation with alcohol had no effect on the melting point of the product, the various fractions melted uniformly at 89°, the melting point of

<sup>1</sup> See the theoretical part.

<sup>2</sup> This result was obtained Nov. 10 and Dec. 8, 1913 (see the introductory footnote to this article).

<sup>3</sup> Jan. 10, 1914.

*p*-bromoazobenzene, whether tested alone or mixed with a known sample of *p*-bromoazobenzene.

Dichlorohydrazobenzene (2 g., 95–96% pure), treated in the same way, yielded on cooling a mass of bright orange needles, which were separated by filtration from the red alcoholic solution, and extracted three times with alcohol. The melting point of the needles was 100°, and this was raised to 103° by the mixing of the crystals with pure dichloroazobenzene (m. p. 105°). The residues from the extractions melted at 105°, as did the crystals obtained by evaporation of the alcoholic filtrates from the last two extractions. Evaporation of the acidified alcoholic solution, and of the alcohol used in the first extraction, gave orange-colored crystals melting below 100°. In no case did admixture of dichloroazobenzene lower the melting point still further, and the impurities which caused the low melting point could hardly have included tetrachloroazobenzene (m. p. 161°), which is but little soluble in alcohol.<sup>1</sup> The more insoluble fractions always had the melting point of 2,4-dichloroazobenzene.

In the determination of the ratio of the two amines formed in the decomposition, the method of precipitation of their hydrochlorides<sup>2</sup> was used, with subsequent bromination with 0.1 *N* potassium bromate solution.<sup>3</sup> Of the three hydrazo compounds studied, *p*-bromohydrazobenzene was most suitable for this purpose, since the two amines from *p*-methylhydrazobenzene have nearly the same molecular weight, and since dichloroaniline is only very slightly basic.<sup>4</sup> A 0.2 molal solution (10 cc.) of bromohydrazobenzene in alcohol was heated at 145° in evacuated tubes for 12 hours; after the tubes had been cooled, their contents were introduced into a distilling flask containing 15 cc. 0.1 *N* HCl, 0.3 g. acid ammonium carbonate, and an excess of 0.1 *N* iodine solution. The oxidation of the undecomposed hydrazo compound by the iodine was thus carried out in the presence of carbonic acid and ammonium acid carbonate, *i. e.*, in a very slightly alkaline medium, and rearrangement of the hydrazo compound under the influence of acid therefore avoided. The mixture was allowed to stand for ten minutes before it was acidified with 20 cc. of 6 *N* sulfuric acid. It was then distilled with steam until the azo compound had all passed over, and the further distillate was colorless. Sodium hydroxide (20 cc. of a 10 *N* solution) was added to the mixture in the distilling flask, and 100 cc. of the liquid were distilled from the alkaline solution into dilute hydrochloric acid. This solution of the amine hydrochlorides was evaporated down to about 25 cc. by dry air drawn through

<sup>1</sup> Zincke, *Ber.*, 34, 2855 (1901).

<sup>2</sup> Stieglitz and Leech, *THIS JOURNAL*, 36, 272 (1914).

<sup>3</sup> Curme, *Loc. cit.*, p. 1162. Cf. also p. 1169 for the less direct method there described in the study of the proportion of the two amines from *p*-methylhydrazobenzene, and the results obtained.

<sup>4</sup> Witt, *Ber.*, 7, 1602 (1874).

it at reduced pressure at  $55^{\circ}$ ; it was then transferred to a separatory funnel, made alkaline with 33% potassium hydroxide solution, and extracted with alcohol-free chloroform until the aqueous layer gave no color with chloride of lime.<sup>1</sup> The chloroform solution was filtered through a cotton plug in the stem of a funnel into a weighed beaker; sodium-dried ether (2 cc.), saturated with hydrogen chloride gas, was added to the chloroform to convert the amines into the hydrochlorides, and partly precipitated them as such; the liquid was evaporated by dry air drawn over the beaker. The hydrochlorides were then dried to constant weight in vacuum over calcium chloride, extracted with 2-3 cc. ligroin to remove any organic impurities, and again weighed to constant weight. The product thus obtained was almost colorless, and was analyzed by bromination as follows: A weighed portion of the mixed hydrochlorides was dissolved in a small amount of water in an Erlenmeyer flask, and 10 cc. 10% potassium bromide solution added to the solution. A definite amount of standard 0.1 *N* potassium bromate was run in from a buret, the flask closed by means of a paraffined cork holding a calcium chloride tube containing glass beads moistened with potassium iodide solution, and the mixture kept in a water bath at  $50^{\circ}$  for fifteen minutes. White tribromoaniline was precipitated out, and the solution was colored yellow by the excess of free bromine. Potassium iodide (10 cc. of a 10% solution) was rinsed through the glass beads, the mixture was cooled, and the end point determined with 0.1 *N* thiosulfate solution and starch indicator. Blank experiments with known amounts of aniline, bromoaniline, bromoazobenzene, and bromohydrazobenzene, corresponding to the amounts present in 10 cc. of a 0.2 molal solution of bromohydrazobenzene after 12 hours' heating, showed that the ratio of amines could be determined by this method with an accuracy of 0.4%.<sup>2</sup> But as there are undoubt-

<sup>1</sup> Ten drops of half-saturated chloride of lime solution will produce a distinct brown color in 3 cc. of a slightly alkaline solution of *p*-bromoaniline containing as little as 2 milligrams of the amine. The ordinary test for aniline can therefore be used to test for both amines in question.

<sup>2</sup> If we put:  $x$  = millimols of aniline hydrochloride used,  
 $y$  = millimols of bromoaniline hydrochloride used,  
 $g$  = weight of mixed hydrochlorides used,  
 $c$  = volume, in cc., of 0.1 *N* bromate used,

then we have:

$$\begin{aligned} 0.1295 x + 0.2085 y &= g \\ 60 x + 40 y &= c \end{aligned}$$

(Cf. Curme, *Loc. cit.*)

A mixture of 0.0728 g. aniline and 0.1449 g. bromoaniline with 0.15 g. bromohydrazobenzene and 0.40 g. bromoazobenzene was run through the entire process, beginning with the oxidation of the hydrazo compound by 0.1 *N* iodine solution. 0.0613 g. of the mixed hydrochlorides required 17.90 cc. 0.1 *N*  $\text{KBrO}_3$ . These analytical data give 48.49 molar % aniline, while there was actually present in the original mixture of amines, 48.14 % aniline.



edly present in the decomposed hydrazo solution, products of benzidine or similar rearrangements which are somewhat volatile with steam from basic but not from acid solution, the error in an actual determination may be larger. In any case, however, it is well within the necessary limit of accuracy. The following results were obtained in two experiments carried out as described:

Gram amine hydrochlorides.	Cc. 0.1 <i>N</i> KBrO <sub>3</sub> .	Molar percentages.	
		Aniline.	Bromoaniline.
0.0627	18.58	50.2	49.8
0.0673	19.63	48.4	51.6

The above experiments establish the fact that there is only one azo compound, the asymmetrical one, found in the thermal decomposition products of asymmetrical hydrazobenzenes; and the further fact that the two amines are found in equimolecular proportions. The interpretation of the reaction involving the formation of phenyl imide radicals must therefore be incorrect.<sup>1</sup>

**3. The Velocity of Decomposition of *p*-Bromohydrazobenzene and 2,4-Dichlorohydrazobenzene.**—In order to justify the assumption that *p*-bromo- and 2,4-dichlorohydrazobenzene would resemble the hydrazo compounds studied by Curme, and give velocity constants according to the law for a monomolecular reaction (see Equation 5), determinations of the velocity of decomposition were carried out with *p*-bromohydrazobenzene and dichlorohydrazobenzene in alcoholic solution. Curme's apparatus and methods<sup>2</sup> were used, the tubes containing the solution being sealed off in a freezing mixture at a pressure of 10–20 mm. The whole number of tubes was then heated to 70–80° in a small oil bath and plunged simultaneously into the thermostat at 145°. On removal from the thermostat after a definite time interval, each tube was plunged into the bath at 70–80° for thirty seconds, cooled to ordinary temperatures by water, and analyzed as soon as convenient. Essentially the same method of analysis was employed as in assaying the pure bromohydrazobenzene, except that no aniline was used. The reason for this change was that in neutral or alkaline solution, a dark discoloration<sup>3</sup> which interfered with the sharpness of the end point, appeared on oxidation of the decomposed hydrazo solution. This was entirely avoided by carrying out the oxidation in slightly acid solution, and accordingly, the acid formed by the decomposition was not neutralized by the addition of aniline nor of acid ammonium carbonate. On the other hand, since aniline is formed by the decomposition, it was found necessary, after the decomposition had been allowed to proceed for some time, to add a small

<sup>1</sup> See Wieland, *Ber.*, 48, 1104 (1915) and the theoretical part of this article.

<sup>2</sup> Curme, *Loc. cit.*, p. 1156.

<sup>3</sup> According to Wieland (*Ber.*, 48, 1104) this is due to some semidine formed when hydrazobenzenes are heated in alcohol solution.

amount of 0.1 *N* HCl solution to the iodine solution before introducing the hydrazo solution, in order to have the oxidation mixture acid, and thus obtain a sharp end point.

The results for *p*-bromohydrazobenzene in 0.2 and 0.05 molal solutions are found in Table I. The first column gives the time in minutes during which the tube was heated, the second and fourth the number of grams of 0.1 *N* iodine solution required for 5 cc. of the hydrazo solution in two separate experiments, the third and fifth the values of the corresponding constants for a monomolecular reaction, calculated from these data and the above equation, and the sixth column the average value of  $K_{\text{mono}}$ . For the sake of comparison, in the last column is given the velocity constant for a dimolecular reaction, calculated from the data given in the fourth column and Equation 7.

It will be noticed that the "constant" for bromohydrazobenzene, while not showing the inclination to droop exhibited by the "constants" for Curme's substances, varies slightly from concentration to concentration. As the first determinations in 0.2 and 0.05 molar concentrations were run simultaneously, the difference in the constant for the two concentrations cannot be ascribed to an unobserved change of temperature of the thermostat.

TABLE I.

0.2 molal solution of *p*-bromohydrazobenzene. Temperature 145° (uncorrected).

Time.	G. 0.1 <i>N</i> I.	$10^3 \times K_{\text{mono}}$ .	G. 0.1 <i>N</i> I.	$10^3 \times K_{\text{mono}}$ .	Average $10^3 \times K_{\text{mono}}$ .	$K_{\text{di}}$ .
90	16.52	...	16.05	...	...	...
150	14.80	183	14.27	196	190	0.0129
210	13.10	192	12.92	181	187	0.0126
300	10.92	197	10.55	200	199	0.0155
450	7.64	214	7.85	199	207	0.0181
510	7.23	197	6.91	201	199	0.0196
600	6.22	192	5.82	199	196	0.0215
720	..	...	4.14	215	215	0.0285

199

0.05 molal solution of *p*-bromohydrazobenzene.

Time.	G. 0.1 <i>N</i> I.	$10^3 \times K_{\text{mono}}$ .	G. 0.1 <i>N</i> I.	$10^3 \times K_{\text{mono}}$ .	Average $10^3 \times K_{\text{mono}}$ .	$K_{\text{di}}$ .
90	4.21	...	4.18	...	...	...
150	3.81	167	3.84	(141)	167	0.0353
210	3.41	176	3.41	170	174	0.0450
300	2.91	176	2.89	176	176	0.0509
450	2.23	177	2.27	170	174	0.0559
510	2.05	171	2.09	165	168	0.0570
600	1.83	163	1.77	169	166	0.0639
720	..	...	1.38	176	176	0.0771

171

Since the original theory of the reaction had to be abandoned as a result of the study of the products of the decomposition (see the theoretica

part), the velocity was next measured in exceedingly dilute solutions in order to determine whether the order of the reaction changes with extreme dilution. •For the analytical data, 0.05 *N* and 0.1 *N* solutions of iodine and sodium thiosulfate were used as indicated, and 10 cc. of the hydrazo solution used for each titration. Whereas the results (Table II) show values for a dimolecular reaction constant within experimental error in any one series, the constant in 0.005 molar is practically three times the constant in 0.01 molar concentration. The values of the monomolecular constant fall off decidedly in any series in these very dilute solutions, but the average value for *all* the concentrations used varies only from  $199 \times 10_5$  in 0.2 molar to  $258 \times 10_5$  in 0.005 molar; while the average value for the dimolecular constant in 0.2 molar is only one one-hundredth of the constant in 0.005 molar (0.0184 to 1.27).

TABLE II.

0.015 molal solution of <i>p</i> -bromohydrazobenzene.						
Time.	G. 0.05 <i>N</i> I.	K <sub>di</sub> .				
90	5.02	...				
150	4.42	0.180				
210	4.00	0.169				
300	3.31	0.196				
450	2.68	0.193				
510	2.36	0.214				
600	2.12	0.214				
720	1.82	0.222				
						183
0.01 molal solution of <i>p</i> -bromohydrazobenzene.						
Time.	G. 0.05 <i>N</i> I.	K <sub>di</sub> .	G. 0.05 <i>N</i> I.	K <sub>di</sub> .	Average K <sub>di</sub> .	10 <sup>5</sup> × K <sub>mono</sub> .
90	2.90	...	2.70	...	...	...
150	2.45	0.420	2.32	0.404	0.412	253
210	2.16	0.394	2.10	0.353	0.374	209
300	1.80	0.401	1.70	0.415	0.408	220
450	1.49	0.363	1.35	0.412	0.388	193
510	1.29	0.410	1.19	0.448	0.429	195
600	1.16	0.406	1.06	0.449	0.428	183
720	0.87	(0.511)	0.98	0.413	0.413	161
						0.407
						202
0.005 molal solution of <i>p</i> -bromohydrazobenzene.						
Time.	0.05 <i>N</i> I.	K <sub>di</sub> .	G. 0.01 <i>N</i> I.	K <sub>di</sub> .	Average.	10 <sup>5</sup> × K <sub>mono</sub> .
90	1.25	...	6.05	...	...	...
150	0.94	1.76	4.91	1.28	1.52	348
210	0.88	1.12	4.03	1.38	1.25	339
300	0.67	1.32	3.99	(0.81)	1.32	(198)
450	0.58	1.03	2.57	1.25	1.14	238
510	0.47	1.26	2.21	1.37	1.32	240
600	0.36	(1.55)	2.18	1.15	1.15	300
720	0.37	1.21	1.89	1.16	1.19	185
						1.27
						258

The order of a reaction is tested more exactly by the constancy or inconstancy of the velocity constant in two solutions of differing initial concentrations, than by its constancy through the course of the reaction in any one solution. An exact expression for the order of a reaction, involving solutions of differing initial concentrations, has been developed by A. A. Noyes:<sup>1</sup>

$$n = 1 + \frac{\ln t_1/t_2}{\ln c_2/c_1},$$

where  $n$  is the order of the reaction, and  $t_1$  and  $t_2$  are the time intervals required for the reaction to proceed to equal fractions of the original concentrations,  $c_1$  and  $c_2$ .

In order to test the reaction in question by means of this equation, the percentages of decomposition in terms of the concentrations after 90 minutes at 145° were calculated from the data in Tables I and II, and the results plotted. The times required for a given percentage decomposition were found from this graph, and the values substituted in Noyes's equation. Tabulation of the results thus obtained will be found in Table III.

TABLE III.

Initial conc., mols per liter. Av. of two values.	Per cent. decom- posed.	Time in minutes.	$n=1+\frac{\ln h/h}{\ln c_2/c_1}$	Initial conc., mols per liter. Av. of two values.	Per cent. decom- posed.	Time in minutes.	$n=1+\frac{\ln' h/h}{\ln c_2/c_1}$
0.1617.	33 <sup>1</sup> / <sub>3</sub>	205	1.10	0.1617	66 <sup>2</sup> / <sub>3</sub>	550	1.04
0.0418	33 <sup>1</sup> / <sub>3</sub>	235		0.0070	66 <sup>2</sup> / <sub>3</sub>	630	
0.1617	50	350	1.11	0.0070	33 <sup>1</sup> / <sub>3</sub>	170	0.63
0.0418	50	405		0.0031	33 <sup>1</sup> / <sub>3</sub>	125	
0.1617	66 <sup>2</sup> / <sub>3</sub>	550	1.11	0.0070	50	350	0.62
0.0418	66 <sup>2</sup> / <sub>3</sub>	635		0.0031	50	235	
0.1617	33 <sup>1</sup> / <sub>3</sub>	205	0.94	0.0070	66 <sup>2</sup> / <sub>3</sub>	630	0.79
0.0070	33 <sup>1</sup> / <sub>3</sub>	170		0.0031	66 <sup>2</sup> / <sub>3</sub>	525	
0.1617	50	350	1.00				
0.0070	50	350					

From these values of  $n$ , there can be no question as to the order of the reaction. The largest values are found for the more concentrated solutions where the velocity constants for a monomolecular reaction are unambiguous; and in these cases, the differences from unity are inconsiderable. Comparison of the two more dilute solutions gives values decidedly below one, which shows that in spite of the constancy of the value of  $K$  for a dimolecular reaction in each of these solutions by itself, the reaction is not dimolecular.

A study of the velocity constants of the decomposition of 2,4-dichlorohydrazobenzene (Table IV), shows that with this substance the monomolecular constant, which remains unchanged through a run in 0.1 molal

<sup>1</sup> Cf. Kremann, *Monatsh.*, 27, 611 (1906).

solution, falls off<sup>1</sup> toward the end of the run in a concentration (0.05 molar) where the constant for bromohydrazobenzene is still good. The average values<sup>2</sup> of the constant for the chlorohydrazo compound agree very well in the two concentrations. In the third and lowest concentration used (0.01 molar), the monomolecular constant falls off still more decidedly, as would be expected from the results with bromohydrazobenzene, but the dimolecular constant, on the other hand, shows a tendency to rise, which is not the case with the bromohydrazo compound in solutions less than 0.015 molal. Just as before with bromohydrazobenzene, the dimolecular constants for dichlorohydrazobenzene vary greatly from concentration to concentration, and this substance supports the evidence against a dimolecular reaction.

TABLE IV.

0.1 molal 2,4-dichlorohydrazobenzene.				0.05 molal 2,4-dichlorohydrazobenzene.			0.01 molal 2,4-dichlorohydrazobenzene.		
Time.	G. 0.1 N I required for 5 cc.	10 <sup>3</sup> X K <sub>mono</sub> .	K <sub>di</sub> .	G. 0.1 N I required for 5 cc.	10 <sup>3</sup> X K <sub>mono</sub> .	K <sub>di</sub> .	G. 0.01 N I required for 10 cc.	10 <sup>3</sup> X K <sub>mono</sub> .	K <sub>di</sub> .
60	7.07	...	....	3.89	...	....	13.61	...	...
120	6.08	251	0.0387	3.25	300	0.0846	10.66	(407)	0.678
180	5.08	276	0.0462	2.72	298	0.0922	9.23	324	0.581
240	4.35	270	0.0491	2.37	275	0.0916	7.79	310	0.610
300	3.59	282	0.0571	2.04	269	0.0971	6.67	297	0.637
390	2.87	273	0.0627	1.57	275	0.0151	5.40	280	0.677
480	2.24	274	0.0726	1.28	265	0.1248	4.36	271	0.742
600	1.71	278	0.0854	1.09	236	0.1220	3.49	267	0.789
720	1.15	275	0.0102	1.07	(196)	(0.1027)	1.53	(347)	(1.766)
		272	0.0652		274	0.1039		292	0.673

**4. Parallel Determinations of Hydrazo Compound Consumed and Amines Formed.**—In Curme's work on hydrazobenzenes, he calculated the velocity constant for the decomposition by means of the increasing amounts of aniline formed, and found that this method of analysis also gave a velocity constant according to the law for a monomolecular reaction, with only a slightly lower value than that obtained from the analytical determinations of the undecomposed hydrazo compound.<sup>2</sup> The method was indirect in that the amount of hydrazobenzene present at any instant of time was *calculated* from the experimentally determined concentration of hydrazo compound at the beginning of the run and the amount of aniline present at the time considered. In the following experiments on *p*-bromohydrazobenzene, the amounts of hydrazo compound as well as the amounts of amine present, were determined *experi-*

<sup>1</sup> A part but not all of this drop of 33 1/3% might be attributed to experimental error. No duplicate determination was made, owing to lack of time and the difficulty of preparing the substance.

<sup>2</sup> Curme, *Loc. cit.*, p. 1163.

mentally in each case; *i. e.*, four tubes, each containing 5 cc. of the solution, were removed from the thermostat at one time, the contents of two of them analyzed as above for bromohydrazobenzene by oxidation with 0.1 *N* iodine, and the contents of the other two for amines by separation through steam distillation as above, and bromination of the acidified distillate with 0.1 *N* potassium bromate. It has already been shown that the two amines occur in equimolecular proportions; the equation for the bromination is therefore



Since two mols of amine are formed by the decomposition of *two* mols of hydrazo compound, one cc. 0.1 *N* potassium bromate corresponds to 0.00002 mol hydrazo compound.

In Table V we find in the first column the time in minutes during which the tubes were heated, in the second the number of grams of 0.1 *N* iodine required for 10 cc. of solution, and in the third the corresponding number of mols of unchanged hydrazo compound per liter, calculated from consideration of the fact that one cc. 0.1 *N* iodine to 10 cc. solution is equivalent to 0.005 mol hydrazine per liter. In the fourth column is given the number of cubic centimeters of 0.1 *N* potassium bromate solution required for 10 cc. of the hydrazo solution, and in the fifth the number of mols hydrazine decomposed per liter. In the last column are given the sums of the concentrations in the third and fifth columns, *i. e.*, the total concentration of the hydrazo compound, decomposed and undecomposed. If there is no interfering reaction by which bromohydrazobenzene is used up without producing amine,<sup>1</sup> the numbers in the last column should be constant. This is the case within the limit of the experimental error, which is rather wide here, since it is the sum of the possible error in the iodine analysis and the error in the bromate analysis.

TABLE V.

Time.	G. 0.1 <i>N</i> I.	Conc. undecomposed hydrazobenzene.	Cc. 0.1 <i>N</i> KBrO <sub>3</sub> .	Conc. decomposed hydrazobenzene.	Total hydrazo conc.
90	8.25	0.04125	4.64	0.00928	0.0505
180	6.82	0.03410	7.23	0.01446	0.0486
270	5.69	0.02845	9.12	0.01824	0.0467
390	4.60	0.02300	12.58	0.02516	0.0482
570	3.40	0.01700	14.71	0.02942	0.0464

Table VI gives, in exactly similar form, the results of duplicate experiments on less concentrated solutions. In neither concentration is there any indication of a secondary reaction which is not negligible, nor is there any difference between the two concentrations.

<sup>1</sup> According to Wieland's work, published since this was written, small amounts of the hydrazobenzene suffer a semidine rearrangement under the conditions used (Wieland, *Loc. cit.*).

TABLE VI.

Time.	G. 0.01 <i>N</i> I.	Conc. undecomposed hydrazobenzene.	Cc. 0.01 <i>N</i> KBrO <sub>3</sub> .	Conc. decomposed hydrazobenzene.	Total hydrazo conc.
90	13.63	0.006815	7.86	0.001572	0.00838
180	11.83	0.005915	12.12	0.002424	0.00834
270	9.83	0.004915	15.00	0.003000	0.00791
390	7.65	0.003825	20.81	0.004162	0.00799
570	6.09	0.003045	25.74	0.005148	0.00819
90	13.88	0.006940	7.47	0.001494	0.00843
180	10.76	0.005380	12.92	0.002584	0.00796
270	9.83	0.004915	16.39	0.003278	0.00819
390	7.66	0.003830	21.14	0.004228	0.00806
570	4.82	0.002410	26.50	0.005300	0.00781

**5. Gaseous Products of Decomposition.**—In order to determine whether any hydrogen could be detected as a product of the thermal decomposition of hydrazobenzenes, an approximately molal solution of *p*-bromohydrazobenzene (10 cc.) was heated for 12 hours at 145° in two tubes which had been sealed off at a pressure of 10 mm. After cooling, the tubes contained a dark blue crystalline mass. When they were opened under a eudiometer filled with water, a very small bubble of permanent gas appeared—perhaps 0.03 cc. from each tube.

Since the solid product of the reaction made it seem possible that the reaction might have gone somewhat differently in this molal solution than in the more dilute solutions used in the velocity experiments, tubes containing 0.05 and 0.01 molal solutions were tested in a similar manner. From a tube containing 5 cc. of either solution with 6.5 cc. free space, which had been sealed off in a freezing mixture at 18 mm., and heated twelve hours at 145°, was obtained 0.7 cc. permanent gas at room temperature. Since the gas contained in 6.5 cc. at 0° and 18 mm. could give only 0.17 cc. at 20° and 760 mm., there must be some gas evolved during the heating, the nature of which was investigated in the following experiment: 50 cc. of 0.01 molal solution of bromohydrazobenzene were sealed off at 18 mm. in a bomb-tube of 125 cc. capacity, and heated for 10 hours at 145°. The tube was then opened under an inverted buret filled with water, and the gas transferred to a gas buret, and tested for hydrogen by passage over palladium black at 95°, after the oxygen present had been removed with pyrogallol. The volume of gas obtained from the tube was 4.6 cc. which was decreased to 4.35 cc. by the pyrogallol absorption. Treatment with palladium black reduced this volume only 0.05 cc.; and a subsequent attempt to explode the gas with the electric spark after admitting 12 cc. of air had no effect whatever. It is therefore certain that the gas obtained is not hydrogen, and that it can contain at most very small quantities of hydrogen, if any; and the small amount of oxygen shows that it cannot have been residual air due to imperfect evacuation

of the tube. There remains the possibility of some slight secondary decomposition of the hydrazo compound which involves evolution of nitrogen.<sup>1</sup>

**6. Effect of Molecular Hydrogen on Hydrazobenzene.**—To exclude the possibility that molecular hydrogen might react with hydrazobenzenes under the conditions of the experiments, an approximately 0.5 molal solution (5 cc.) was sealed off in a tube suspended in ice, with a stream of hydrogen at atmospheric pressure passing through it. The tube was then heated for two hours at 145°, cooled, and opened under a eudiometer. The volume of permanent gas obtained over water at 20° was 18.9 cc., while the volume of the tube above the solution was 17.15 cc.; 18.9 cc. at 20° corresponds to 18.2 cc. at 10°, which is about the temperature at which the tube was sealed off. Roughly, therefore, 1 cc. excess gas was found, and no appreciable amount of hydrogen was consumed by the hydrazo compound.

**7. Molecular Weight in Alcoholic Solution.**—There still remained the possibility that association of the hydrazo compound might account for the fact that the decomposition appeared as a monomolecular reaction, and that the decomposition of these complex molecules was the reaction of which the velocity was measured. The molecular weight of *p*-bromohydrazobenzene in absolute alcohol was therefore determined, and the evidence obtained was decisively against any association, as Table VII shows. McCoy's boiling point apparatus was used. In the following tabulation of the results, the first column contains the observed change in boiling point ( $\Delta$ ), the second the corresponding volume ( $V$ ) of solution in which the given weight ( $W$ ) of substance was dissolved, and the last column the molecular weight calculated from these data by means of the equation:

$$\text{Molecular weight} = \frac{W \times T}{\Delta \times V},$$

where  $T = 1560$  for alcohol.<sup>2</sup> The concentration of the solution at the beginning of the experiment was approximately 0.2 molar.

TABLE VII.

$W = \text{grams } p\text{-bromohydrazobenzene taken} = 0.8403.$

$\Delta$ .....	0.185°	0.173	0.175	0.170	0.172	0.161	0.161
Vol. in cc. ....	25.7	26.9	27.6	28.3	29.7	32.7	33.0
Mol. wt. ....	276	282	271	272	257	249	247
						Av., 265	
						Calculated for $C_6H_4NH.NHC_6H_4Br$	263

CHICAGO, ILL.

<sup>1</sup> These conclusions have been fully confirmed since by E. N. Roberts in this laboratory (see footnote 3, p. 1741).

<sup>2</sup> McCoy, *Am. Chem. J.*, 23, 353 (1900).



[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA.]  
**A CATALYTIC DECOMPOSITION OF CERTAIN PHENOL SILVER SALTS.**

[FIRST PAPER.<sup>1</sup>]

By W. H. HUNTER, A. O. OLSON AND E. A. DANIELS.

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During the progress of work on the chromoisomeric silver salts of some halogenated phenols, it was observed by Torrey and Hunter<sup>2</sup> that both the red and white silver salts of tribromophenol, if absolutely dry, reacted in a very unusual way with dry undiluted ethyl iodide. The iodide solutions rapidly assumed a deep blue color, which faded a little more slowly, giving way to a brownish yellow. A precipitate remained which consisted mainly of silver bromide with a little iodide, while the ethyl iodide held in solution a white amorphous compound, which could be precipitated by alcohol. This compound could also be obtained by the use of other alkyl iodides, but the different preparations were practically identical in bromine content, showing that no alkyl group had been introduced. Direct tests showed a complete absence of silver and iodine.

At this point the work was dropped, as it offered no immediate assistance in the study of the silver salts. The reaction possessed considerable intrinsic interest however, because it was so different in all respects from the expected alkylation. On this account, work on the change has since been taken up in this laboratory, and the present paper embodies that part of the work which is concerned with the composition of the white amorphous compound, the preparation of analogous compounds, their genetic relation to the parent silver salts, and the nature of the reaction by which they are formed.

**The Composition of the White Amorphous Compounds.**—On taking up the work again, the amorphous compound from tribromophenol was analyzed for carbon and hydrogen, and its molecular weight was determined cryoscopically, when it was found that it possesses the formula  $(C_6H_2Br_2O)_n$ . Its physical properties are entirely in accord with this formula, as it is completely amorphous, and very soluble in organic liquids containing halogen, but swells up before dissolving, and on evaporation of the solvent is left as a yellow-brown varnish. Slowly heated in a melting point tube, it commences to shrink at about 260°, gradually sintering and turning darker, until at about 290° it is almost black. On account of these properties it could only be purified by alternate solution in ethyl iodide or chloroform, and reprecipitation with alcohol, and its purity could only be tested by analysis of successive fractions obtained

<sup>1</sup> Some of the work described in this paper was presented in abstract at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

<sup>2</sup> THIS JOURNAL, 33, 204 (1911).

in this manner. Until further information as to its constitution can be brought forward, it is suggested that it be called polydibromophenylene oxide.<sup>1</sup>

Having ascertained the composition of the white amorphous compound, it became necessary to find out whether other compounds of analogous properties could be obtained from other phenols in like manner. For this purpose, as most like the tribromophenol, were chosen the symmetrical trichlorophenol, and the tribromoresorcinol monomethyl ether, which differs from tribromophenol only by a methoxyl group.

The silver salt of the last named phenol was found to behave in exactly the same way with alkyl iodides as that from tribromophenol, except that the blue color was more persistent. The oxide from this phenol proved to have a bromine content and molecular weight corresponding to that expected, and may be called polydibromomethoxyphenylene oxide. This silver salt soon proved to be very much better suited to a study of the decomposition than the tribromophenolate. For instance, simple covering of the salt with pure benzene is sufficient to induce the whole series of changes, starting in with the blue color, and ending with the formation of a solution of the amorphous oxide, which could be isolated by precipitation with gasoline.

On the other hand, silver trichlorophenolate gave but a slight abnormal reaction with cold ethyl iodide, forming almost no amorphous compound, but yielding trichlorophenetol instead. However, a short heating in benzene brought about the smooth decomposition of the salt, and there was obtained an oxide in every respect analogous to the others.

**The Equation for the Reaction.**—In these three cases, then, a compound had been obtained of a composition corresponding to the original silver salt minus a molecule of silver halide, but of very high molecular weight. In order to see if there might be any other products formed, a weighed sample of the silver salt from the resorcinol derivative was allowed to stand with cold ethyl iodide, and the reaction product was investigated. It was found that within the limit of error of the experi-

<sup>1</sup> This compound is probably identical with that obtained by Kastle and Loevenhart (*Am. Chem. J.*, **27**, 34 (1902)) by the action of sunlight on a solution of tribromophenolbromide. To this compound, though colorless, Kastle and Gilbert (*Am. Chem. J.*,

**27**, 52 (1902)) ascribe tentatively the formula 
$$\text{O} = \text{C} \begin{array}{c} \text{Br} \quad \text{H} \\ \diagup \quad \diagdown \\ \text{C} = \text{C} \\ \diagdown \quad \diagup \\ \text{C} = \text{C} \\ \diagup \quad \diagdown \\ \text{Br} \quad \text{H} \end{array} \text{C} = \text{C} \begin{array}{c} \text{H} \quad \text{Br} \\ \diagup \quad \diagdown \\ \text{C} = \text{C} \\ \diagdown \quad \diagup \\ \text{C} = \text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \text{Br} \end{array} \text{C} = \text{O}$$

which is analogous to the formula now ascribed to the red compound known variously as "Lautemann's red," "diiodo phenylene oxide," and "tetraiodo diphenylene quinone." (Cf. Wilsie, *J. Soc. Chem. Ind.*, 1910.) These interesting relationships will be discussed in a future paper.

ment, the silver salt had been quantitatively transformed into amorphous oxide and tribromoresorcinol methyl ethyl ether, no other products being found.

Obviously, then, the ethyl iodide does not appear in the equation for the formation of the oxide, which will be as follows for the case of the silver tribromophenolate:



**The Mechanism of the Decomposition.**—An attempt at accounting for this action led to the formation of the following hypotheses:

1. The reaction may be intermolecular, the silver atom of one molecule uniting with a bromine from another molecule of the salt, to split out silver bromide and form a chain of rings.
2. The intermolecular reaction may be confined to two molecules, or a very few, which give a residue of low molecular weight, which polymerizes.
3. There may be an "intermediate addition" of alkyl halide, with the formation of a blue compound, and a subsequent splitting out of silver halide and alkyl halide. This would mean the formation of a simple molecule which could polymerize to the white oxide.
4. The decomposition may be strictly intramolecular, a decomposition of the silver salt itself, the silver atom uniting with a bromine atom from its own molecule, to leave the simple residue, which then polymerizes to form the oxide.

The hypotheses concerned with intermolecular reactions seem to be eliminated by the following considerations:

1. The silver salt of the resorcinol derivative decomposes on wetting with benzene, which has very little solvent action on silver salts.
2. Ethyl iodide in vapor form acts on dry salt as if diluted with a solvent such as ether, bringing about an alkylation, with no decomposition. Evidently liquid ethyl iodide is necessary for the new change. It is equally unlikely that the salt dissolves in ethyl iodide.
3. There is no reason for supposing that silver could easily remove halogen attached to the ring, even if the salt were dissolved. Slight solution is more probable in alcohol, where ethyl iodide gives a normal alkylation.
4. There is no silver in the amorphous oxide, or in the blue resins left on evaporation of benzene solutions of the fresh reaction product. It is hard to see how every atom of silver could be removed from the amorphous compound by an intermolecular reaction, which would be expected to leave a silver atom on one end, and a bromine atom on the other end of a long chain of rings.

The next hypothesis, of an addition compound, was easily disposed of by showing that the smooth decomposition could be brought about by heat alone, or by warming to a slightly lower temperature, and "setting

off" the salt with a minute amount of a reactive substance such as ethyl iodide or chlorine. The reaction would then proceed by its own heat, which proved to be sufficient to raise the temperature of one sample from 100° to 180°.

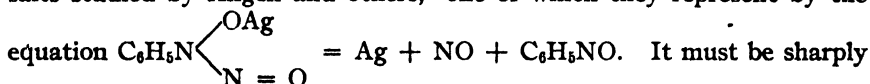
Samples of the oxide produced at these high temperatures were analyzed for bromine. They proved to have a slightly lower content than the theoretical, giving a little over 1% less than the required amount of bromine. It is more surprising that the result should be so close than that a difference should exist, because it must be supposed that more deep-seated changes would certainly occur at the temperatures reached in the decomposing mass of salt, and it would probably be especially difficult to remove such products entirely from the oxides. Nevertheless, there can be no doubt that even at this relatively high temperature, the formation of silver bromide and amorphous oxide is practically the only reaction occurring. A quantitative determination of reaction products proved impossible in this case, on account of the extreme fineness of the silver bromide formed, which became suspended in colloidal form in all solvents, and rendered the purification of the oxide very difficult. No other products than bromide and oxide, however, could be demonstrated in the reaction mixture, and only the low halogen content indicated the presence of other reactions.

These results show conclusively that the reaction can be brought about without any solvent, by heat alone. They also show that reactive substances have a fuse-like action on salt which is heated to a temperature just insufficient to bring about decomposition of the type studied.

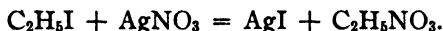
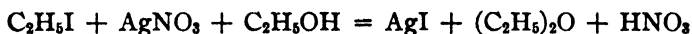
This fuse-like action is probably entirely analogous to the decomposition at low temperatures, which is seen in its extreme form in the decomposition of the silver salt of the monomethyl ether of tribromoresorcin on covering with thiophene-free benzene in a desiccator. Light is apparently not necessary for this change, as it starts first in any deep crack in a lump of salt, which on being opened, will be found completely filled with blue solution. It seems to be due to contact of the benzene with the salt, so that we have the unusual case of a liquid catalyzing a change occurring in a homogeneous solid. Since the deep color is reminiscent of Vorländer's addition compounds of type A, it may be well to insist again upon the absence of silver in the blue varnishes obtained, and upon the fact that the color of these varnishes goes over completely into the light yellow of the amorphous resin left by solutions of the oxides. Further, the action of ethyl iodide vapor in giving the ether instead of the amorphous oxide, while benzene causes the oxide formation, seems to indicate that the presence of actual liquid is more important than the chemical individual it represents. Up to the present time, no experiments have been devised, which can settle the question as to whether the solid dissolves somewhat,

the reaction then occurring in solution, or whether strong adsorption of the benzene or ethyl iodide occurs, followed by decomposition of the surface layers of the solid. This is one of the most interesting points about the change, and it is hoped that some way may be found by which the precise action of benzene may be established. It would be especially interesting in view of Langmuir's late work on adsorption and heterogeneous reactions, on account of the fact that the crystalline white silver salt of tribromophenol reacts just as does the apparently amorphous red form. It does not seem wise to take up this phase of the problem until all other parts of the work shall have been cleared up as far as possible.

The reaction is somewhat like those smooth decompositions of silver salts studied by Angeli and others,<sup>1</sup> one of which they represent by the



contrasted with that of Burke and Donnan,<sup>2</sup> who found that alkyl halides in alcohol act on silver nitrate to give two reactions, represented by the equations



Several interesting problems are raised by the acceptance of the simple decomposition, some of which are still being investigated. It seems worth while to mention two of them at this point.

The first one is that of the blue color. So far, no expedient has been devised, which permits the isolation of a blue compound. All the data so far at hand lead to the view that the blue compound is a polymer of the unsaturated residue, lower than the white oxide—even conceivably the unsaturated residue itself—or that it may be related to coerulignone.

Far more important is the following problem: If the hypothesis of a simple monomolecular reaction is correct, how can it be brought about in one case by heat, in another case by a reactive substance such as ethyl iodide, that can and does react with other molecules of the phenolate at the same time, and in yet a third case by a substance, benzene, which presumably does not react with it in the ordinary sense of the word?

It may, perhaps, be temporarily viewed as a result of at least two factors, of which one is the known instability of silver salts, and the other the presence in the molecule of a benzene ring loaded with halogen atoms in the critical ortho and para positions. It may be conceived that in such a molecule, the silver atom would be unusually closely related to one of the halogens, whether by being actually on the same carbon atom, as sug-

<sup>1</sup> Angeli and Alessandri, *Atti accad. Lincei*, 18, 38 (1909); 18, 784 (1910); Angeli and Marchetti, *Ibid.*, 17, 695 (1908).

<sup>2</sup> *Trans. Chem. Soc.*, 85, 555 (1904); *Zeit. physik. Chem.*, 69, 148 (1909).

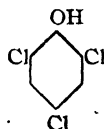
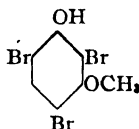
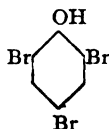
gested for the colored forms by Torrey and Hunter,<sup>1</sup> or better in some other way, which could be equally applicable to all of these salts. In such a molecule there would be considerable tendency for decomposition to occur in such a way as to split out silver bromide in just such a manner as occurs with our salts. In other words, there would be a strain in the molecule, which would not be sufficient to bring about a spontaneous decomposition of the pure dry salt, but which would determine the line of fission of the molecule when gently heated.

When the salt is not heated, but is covered with benzene, the effect of solution, or, as has been already suggested, of adsorption—in either case, the intimate approach of molecules of liquid and salt, must bring about changes comparable to those of ordinary surface catalytic effects—perhaps comparable more nearly to Baly's ideas of chemical change.

Further work is in progress along several lines opened up by this view of the salts and their decomposition, which is intended to serve at present simply as a working hypothesis.

### Summary.

The silver salts of the following phenols



suffer a smooth decomposition into silver halide and an amorphous polymerized residue, in the sense of the following equation:



This occurs readily on suspension of the salt in alkyl iodides, or in pure benzene.

The same effect is produced by heating to temperatures slightly above 100°.

It is suggested by the authors that this may be due to a stress existing in the molecule of the silver salt; between the silver atom and the halogen which goes out with it, not sufficient to cause decomposition until some catalytic effect is exerted on the molecule from without.

### Experimental Part.

**Preparation of the Silver Salts of the Phenols.**—Since the phenols used are but slightly soluble in water, but give soluble alkali salts, quite strongly hydrolyzed, the following procedure has been used for the preparation of their silver salts:

The pure phenol was dissolved in a slight excess of twice normal potassium hydroxide solution, as free from halogen as possible, and after considerable dilution 1% acetic acid was added to the mixture with

<sup>1</sup> *Loc. cit.*

stirring, until a slight permanent precipitate of the phenol was obtained, indicating a neutralization of the excess alkali. A few drops of very dilute silver nitrate were then added, and the solution was well stirred to insure opportunity for the precipitation of any halogen ion present.

The mixture was then allowed to stand for a while, and filtered without suction. A clear bright solution resulted, which gave a voluminous precipitate of the desired silver salt on addition of silver nitrate. The silver salts of the three phenols used in this work were all known—the one from trichlorophenol is yellow, the one from tribromoresorcinol monomethyl ether is white, and the one from tribromophenol is one of Torrey's<sup>1</sup> silver salts, and exists in two modifications, a red and a white.

This precipitate was allowed to stand in the dark for an hour or more, to allow it to become granular, and then filtered without suction, with washing on the filter till the wash water gives only a slight opalescence on testing for silver—the silver salts themselves are slightly soluble in water. It was then transferred to a Buechner funnel, sucked dry, partly dried by continuing the suction, and transferred to clean glass watch glasses, spread out thin. It was allowed to dry by standing in clean air in the dark, and finally in a desiccator in the dark, best over calcium chloride. In this way very pure samples of silver salts were obtained, which could be kept for a long time without signs of change.

**Experiments with Tribromophenol Derivatives.**—Some of the polydibromophenylene oxide was made by the action of ethyl iodide on the red silver salt of tribromophenol, as described by Torrey and Hunter.<sup>2</sup>

Subst. 0.2187; CO<sub>2</sub>, 0.2348; H<sub>2</sub>O, 0.0199. Subst. 0.1500; AgBr, 0.2260.

Calc. for C<sub>6</sub>H<sub>2</sub>Br<sub>3</sub>O: C, 28.81; H, 1.02; Br, 63.99. Found: C, 29.28; H, 1.02; Br, 64.12.

The silver halide from the Carius determination was treated with zinc and sulfuric acid, and the solution tested for iodide with chloroform and bromine water, but none was found.

**Molecular-weight Determination.** This was carried out with recrystallized bromoform as solvent.  $K = 144$ . (Freezing point.)

Solvent, 30.19 g.; subst. 0.207, 0.332;  $\Delta$ , 0.008°, 0.024; Mol. wt., 12,400, 6,600.

**Decomposition of Silver Trichlorophenolate.**<sup>3</sup>—About two grams of the silver salt were placed in an Erlenmeyer flask with 50 cc. of benzene, and the mixture was heated under a reflux condenser on a water bath at 60° for about thirty minutes. The solid remaining at the end of this time was light gray in color, and very finely divided. A great deal of trouble was encountered in obtaining a clear solution, but this was finally accomplished by many filtrations without suction. The clear benzene solution

<sup>1</sup> Torrey and Hunter, *THIS JOURNAL*, **33**, 194 (1911); *Ber.*, **40**, 4322 (1907); Hantzsch, *Ibid.*, **40**, 4875 (1907); Kruyt, *Ibid.*, **43**, 543 (1910).

<sup>2</sup> *THIS JOURNAL*, **33**, 204 (1911).

<sup>3</sup> The work on trichlorophenol was performed by Mr. L. Karatz.

was then completely precipitated by gasoline. An amorphous compound entirely similar in appearance to the one from tribromophenol was obtained, which was purified by alternate solution and reprecipitation with benzene and gasoline and analyzed for chlorine.

Subst. 0.1236, 0.1030, 0.2186 and 0.2008; AgCl, 0.2221, 0.1804, 0.3896 and 0.3565.

Calc. for  $C_6H_2Cl_2O$ : Cl, 44.09. Found: 44.74, 43.61, 44.11, 43.98. Av. = 44.11.

**Action of Ethyl Iodide.**—The chief effect of ethyl iodide is the formation of the trichlorophenetol. Very little amorphous oxide can be obtained in this way, but it can be demonstrated as a reaction product.

**Work on the Silver Salt of Tribromoresorcinol Monomethylether.**

**Decomposition by Ethyl Iodide.**—On covering the dry salt with ethyl iodide the characteristic blue color developed very much more quickly than with the tribromophenol salt, and lasted very much longer. The amorphous white compound was easily obtained by precipitating it with alcohol, though it was at first colored green by adhering blue compound.

Subst. 0.1486; AgBr, 0.1998. Calc. for  $C_6H(OCH_3)Br_2O$ : 57.11. Found: 57.25.

In order to see if any other products were formed, than silver bromide, iodide, the oxide, and the methyl ethyl ether of tribromoresorcinol, 0.811 g. of the salt was covered with pure ethyl iodide, and allowed to stand twenty-four hours. The mixture was then separated by filtration, and the silver salts were washed well, the filtrate and washings being received in a weighed beaker.

The residual silver salt weighed 0.361 g.

The mixture of oxide and ether was heated in the flask in boiling water, but could not be brought to a constant weight, apparently because of slow volatilization of the ether, which crystallized out on the walls of the flask. The observed weight of these products was 0.546 g. No products other than ether and oxide were found.

Now, if all the salt had been converted into oxide and silver bromide, the latter would have weighed 0.326 g., and the oxide, 0.485 g.

This excess in weight of silver residue is due to the weight of iodine in excess of the equivalent bromine,  $I - Br = 0.35$  g.

The total excess weight of both residues is equal to the whole of the ethyl iodide added to the salt, and is 0.096 g.

Calculated from the silver residue, this should be 0.116 g., if only these two reactions occurred.

This is two centigrams of error in ninety-one centigrams, not twenty per cent. of error, and since a loss of the phenol ether from the organic residue would account for part of this, by diminishing the total excess weight, it is not surprising that the result is not closer. Also, some silver bromide might have been transformed into iodide by standing twenty-four hours in ethyl iodide, and this would have increased the silver residue,



but would also have increased over much the calculated weight of ethyl iodide added. Further, no other products have ever been isolated from these reaction mixtures.

**Tribromoresorcinol Methyl Ethyl Ether.**—This is formed at the same time as the amorphous oxide, and can be obtained from the filtrate after precipitation of the oxide by alcohol. Long, hard needles from alcohol and water. Melts at  $75^{\circ}$ . Soluble in ordinary solvents.

Analysis for bromine:

Subst. 0.2593 and 0.3251; AgBr, 0.3756 and 0.4700.

Calc. for  $C_6HBr_3(OCH_3)(OC_2H_5)$ : 61.67. Found: 61.64, 61.50.

#### Molecular-weight Determination on the White Oxide.

This was carried out, using benzene as solvent, by the cryoscopic method. Solvent, 16.0 g. Subst. 0.3530,  $0.2573$ ;  $\Delta$   $0.049^{\circ}$ ,  $0.011^{\circ}$ . Mol. wt. 2250, 7308.

#### Decompositions at Low Temperatures.

**Silver Salt of Tribromoresorcinol Monomethyl Ether:** *Action of Benzene.*—A pure, dry sample of silver salt was covered with thiophene-free benzene, and placed in a calcium chloride desiccator. In a short while a blue color developed, starting first at the larger lumps, and then diffusing away into the solution, which finally became very deep blue. No particular catalytic effect seemed to be exerted by the blue in solution. It was filtered from the solid residue, and the filtered solution was allowed to evaporate at ordinary temperature. The blue color slowly disappeared, and when the benzene had evaporated, a reddish yellow varnish was left, which had all the properties of the amorphous oxides.

A most interesting observation was made on a very pure sample of silver salt, which was washed as usual, and then heated with benzene before it had become entirely dry. The blue color appeared in this case also, and rather rapidly. Another pure sample was then heated with benzene. The blue color appeared immediately, and the same cycle of changes occurred, in much more rapid sequence. The filtered benzene solution, after disappearance of the blue color, gave a copious white precipitate of amorphous substance on the addition of either alcohol or ligroin.

*Cold Ethyl Iodide Vapor.*—0.1927 g. of dry salt was placed in a watch glass, and this suspended in a beaker a couple of inches above the bottom, which was covered with ethyl iodide. It was allowed to stand about seventeen hours, removed to the balance case, and weighed in one hour. It had gained 0.0471 g. in this time. Calculated gain for complete ether formation, 0.0642 g.

On investigation of the product, it was found that no recognizable amount of amorphous compound was present, but that the methyl ethyl ether of tribromoresorcinol was present.

*Ethyl Bromide.*—Some very pure ethyl bromide was made free from alcohol and ether and used soon after its manufacture.

It gave *no* blue color with Torrey's silver salts from tribromophenol on standing.

A sample of the silver salt of tribromoresorcinol monomethyl ether was covered with the ethyl bromide, and placed in a desiccator. After a time, the blue color developed where the salt was piled up highest.

Another sample partly in lumps was placed in the ethyl bromide without crushing. The blue color appeared first in the lumps.

It is interesting that ethyl bromide appears to stand nearer to benzene in its catalytic action than to ethyl iodide.

#### Decompositions at Higher Temperatures.

A thin layer of the silver salt was placed in a narrow porcelain boat about five inches long, and this was placed in the inner tube of a condenser. Steam was passed through the outer jacket of the condenser, and a thermometer was introduced near the salt. It soon registered over  $90^{\circ}$ , and in seven minutes had reached  $99.5^{\circ}$ . It was removed, and the salt heated about a minute longer. Then a flask containing pure ethyl iodide was attached to the condenser, and warmed. Immediately, even before the ethyl iodide had started to boil, a greenish blue patch appeared on the salt nearest the ethyl iodide. In a second or two, the blue color changed to a dull brown, and then this color spread rapidly away from this end of the boat, in one experiment requiring about five seconds to go twenty-five millimeters. An entirely solid residue was left in the boat, though the reaction was accompanied by a curious appearance of fusing or sintering of the salt. Fine particles were also seen to fly up a little distance from the mass, so several samples were weighed out, to see if any amount of substance was being lost in this way, or as a gas.

0.7455 g. lost 0.0047 g. 0.8390 g. lost 0.0032 g. 0.6540 g. lost 0.0051 g.

Another weighed sample was heated alone, without treatment with ethyl iodide. It did not decompose.

0.4426 g. gained 0.0018 g.

It was then treated with iodide vapor as the other samples, when it decomposed, and gained 0.0013 g. more.

The same experiments were tried, using chloroform vapor instead of steam, and the same decomposition was found to occur.

Another sample was lightly packed into a pear-shaped bulb made from a test tube, and a thermometer bulb was inserted into the middle of the salt. It was then heated with live steam until the thermometer registered  $99.5^{\circ}$ , when a very small amount of ethyl iodide was squirted into the bulb so as to touch the silver salt. This decomposed immediately as before, and very soon the temperature commenced to rise, until it reached a maximum of  $185^{\circ}$ .

**Experiments in Tubes.**—Pieces of ordinary glass tubing, 125–150 mm. long, were sealed at one end and cleaned thoroughly. One was filled

with silver salt, and then placed in the steam jacket. After five minutes of heating, the ethyl iodide was let in. The expected green patch appeared at the open end, and then the decomposition proceeded through the tube as in the boat.

Another tube was half filled with silver salt, a layer of sand was placed on it, four or five millimeters in thickness, and the rest of the tube was then filled with more silver salt. The reaction proceeded to the sand only.

In another tube, even less sand was used, the layer being but two or three millimeters thick, in order to avoid contact between the two divisions of the salt. The action again ceased at the sand.

Several samples of these residues were combined and extracted with benzene. This solution was treated with fullers' earth, filtered, and ligroin was added to the reddish solution, when a pink precipitate was obtained. This was redissolved in benzene and reprecipitated six times, and the final product, still slightly pink, was analyzed for halogen.

Subst. 0.1655 and 0.1595; AgBr 0.2179 and 0.2100.

Calc. for  $C_4H(OCH_3)Br_2O$ : Br, 57.11. Found: 56.03, 56.03.

#### Effect of Other Substances.

The following substances, in small amounts, were found to cause the decomposition of preheated salt: Propyl bromide, chloroformic ester, concentrated hydrochloric acid, fuming nitric acid, iodine, and bromine.

MINNEAPOLIS, MINNESOTA.

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### HYDRAZINO DIACIDS.

By J. R. BAILEY AND L. A. MIKESKA

Received June 12, 1916.

#### Introduction.

The first hydrazino diacid, hydrazinodiacetic acid,  $NH_2N(CH_2COOH)_2$ , was discovered in the Heidelberg laboratory by Curtius and Hussong.<sup>1</sup> The method of preparing this substance was improved by Bailey and Read and its reactions further investigated.<sup>2</sup> Darapsky and Prabhakar have announced the discovery of hydrazinodimalonic acid,<sup>3</sup> the second hydrazino diacid thus far reported, but the work described in this article shows that the proofs deduced for the constitution of this substance are not valid.

Hydrazinodiacetic acid is readily made by the action of monochloroacetic acid on hydrazine in alkaline solution, and as the product is difficultly soluble in water, its isolation presents no difficulty. It might be expected that other halogen acids would produce similar results with hydrazine, and that the solubilities in water of the hydrazino diacids thus formed

<sup>1</sup> *J. prakt. Chem.*, [2] **83**, 249 (1911).

<sup>2</sup> *THIS JOURNAL*, **36**, 1748 (1914).

<sup>3</sup> Moreswar Prabhakar, *Dissertation*, Heidelberg, 1912.

would also render them easily separated from the inorganic admixtures produced in their preparation. The other common  $\alpha$ -halogen acids react beyond question on hydrazine in alkaline solution, but on neutralizing the reaction mixtures there is no separation of the expected hydrazino diacids. It might be supposed that, even were the hydrazino diacids readily soluble in water, their isolation could be effected by converting them to the corresponding benzylidene compounds, since all hydrazines, as a rule, readily condense with aldehydes and ketones in the well-known way. However, Curtius and Hussong failed to produce a reaction between hydrazinodiacetic acid and aldehydes as is evidenced by the following quotation from the article referred to above:

"Alle Versuche, die Säure mit Aldehyden zu kondensieren, verliefen ohne Ergebnis. Angewandt wurden: Benzaldehyd, Salicylaldehyd, *m*-Chlorbenzaldehyd, und *m*-Nitrobenzaldehyd. Weder in neutraler, noch in saurer oder alkalischer wässriger Lösung, weder beim unmittelbaren Zusammenbringen der Körper bei gewöhnlicher Temperatur, noch beim Erwärmen trat Kondensation ein."<sup>1</sup>

This peculiar anomaly of hydrazinodiacetic acid, as reported by the German investigators, induced us to institute experiments aimed at establishing conditions under which hydrazinodiacetic acid could be made to react normally with aldehydes. Contrary to the observation of Curtius and Hussong, we find that benzaldehyde reacts smoothly and normally with hydrazinodiacetic acid in aqueous solution, giving a practically quantitative yield of benzylidenehydrazinodiacetic acid, while in potassium hydroxide solution both benzaldehyde and salicylaldehyde condense with this hydrazine, giving hydrazones that can be isolated in the form of the difficultly soluble monopotassium salts. Attention may be directed to the fact that, if neutral potassium hydrazinodiacetate be condensed in water solution with benzaldehyde and then sufficient sulfuric acid added to neutralize all the potassium, the hydrazone separates partly as monopotassium hydrazinodiacetate,



and partly as the free hydrazone acid. The hydroxybenzylidene compound, prepared similarly, separates only in the form of its monopotassium salt. In other words, these potassium salts are stable in the presence of a mineral acid.

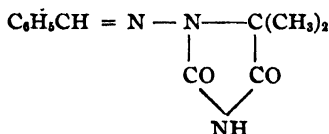
The discovery of hydrazone derivatives of hydrazinodiacetic acid gave an incentive to attempts in the preparation of other hydrazino diacids. The method of Curtius and Hussong, as modified and improved by Bailey and Read,<sup>2</sup> can be extended to the preparation of other hydrazino diacids than the diacetic acid derivative, where the acid rest is of a single type. In the case of mixed hydrazino diacids, such as hydrazinodiacetic-propionic

<sup>1</sup> *J. prakt. Chem.*, [2] 83, 275 (1911).

<sup>2</sup> *Loc. cit.*

acid, the method, for obvious reasons, would not be available. This latter purpose can be effected, as shown in this article, by the reduction of mixed nitrosimino diacids, a reaction employed by Bailey and Snyder<sup>1</sup> in the conversion of nitrosiminodiacetic acid to hydrazinodiacetic acid. Furthermore, in the experimental part of this article it is shown that benzylidenehydrazino monoacids are very reactive in alkaline solution toward  $\alpha$ -halogen acids. By this method both benzylidenehydrazinoacetic-propionic acid, and benzylidenehydrazinodipropionic acid were prepared from benzylidenehydrazinopropionic acid,  $C_6H_5CH = NNHCH(CH_3)COOH$ . Benzylidenehydrazino-*i*-butyric acid,  $C_6H_5CH = NNHC(CH_3)_2COOH$ , was converted similarly by this process to benzylidenehydrazinoacetic-isobutyric acid.

Bailey and Read,<sup>2</sup> and before them Busch and Walter,<sup>3</sup> showed that the imino hydrogen in hydrazones is reactive; the former added cyanic acid on to benzylidenehydrazino-*i*-butyric acid, producing 5-dimethyl-1-benzylideneaminohydantoin,



while the latter investigators with carbonyl chloride and benzylidenephénylhydrazine made benzylidenephénylhydrazinocarboxylic acid chloride,  $C_6H_5CH = NN(COCl)C_6H_5$ . In this article it is shown that cyanic acid in glacial acetic acid with benzylidenehydrazinopropionic acid yields methylbenzylideneaminohydantoinic acid,  $C_6H_5 - CH = NN(CONH_2)CH(COOH)CH_3$ . This observation may lead to a serviceable method of preparing unsymmetrical substitution products of phenylhydrazine, by the introduction of various acid rests on the  $\alpha$ -nitrogen.

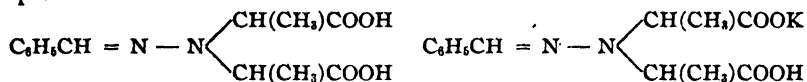
In the work herein described the very unexpected observation has been made that the benzylidene compounds of the hydrazino diacids, with the exception of hydrazinodiacetic acid, on being precipitated from alkaline solution, even with a mineral acid in excess, retain a *half atom* of alkali metal. Benzylidenehydrazinoacetic-propionic acid, benzylidenehydrazinoacetic-isobutyric acid, and benzylidenehydrazinodipropionic acid, when precipitated from either potassium or sodium hydroxide solution, give beautifully crystallizing, snow white substances, on which careful determinations of C, H, N, and K, or Na, give concordant results for the above constitution. These peculiar alkali derivatives, which separate in the presence of an excess of mineral acid, can be recrystallized from glacial acetic acid unchanged. In an experiment with the potassium

<sup>1</sup> THIS JOURNAL, 37, 935 (1915).

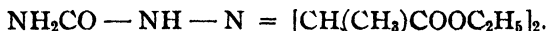
<sup>2</sup> *Ibid.*, 37, 1892 (1915).

<sup>3</sup> *Ber.*, 36, 1359 (1903).

compound of benzylidenehydrazinoacetic-isobutyric acid the hydrazone was suspended in water, the calculated amount of sulfuric acid added to convert all the potassium present to potassium sulfate and solution effected by boiling. The solution was boiled for half an hour with steam passing through it. A part of the benzaldehyde in this process was eliminated, but on cooling a large part of the unchanged potassium salt crystallized out. As was to be expected, the liquid proved strongly acid toward congo paper. The formulas of these alkali derivatives, which are similar to potassium tetroxalate in their constitution, may be exemplified by the following interpretation of the potassium salt of benzylidenehydrazinodipropionic acid:



Experiments to obtain the three new hydrazino diacids in a form suitable for analysis were abandoned, because of their hygroscopic nature. Preliminary experiments have shown that they can be prepared in solution by converting the alkali salts of the benzylidene derivatives into the alcohol soluble sulfates of the hydrazinodiacids and removing the sulfuric acid in the usual way. When precipitated from an alcoholic solution with ether, these hydrazines quickly deliquesce on exposure to air. Their hydrazine nature is revealed by the fact that they condense normally with benzaldehyde like hydrazinodiacetic acid. The structure of hydrazinodipropionic acid has also been confirmed by converting it to ethyl semicarbazinodipropionate,



The benzylidene derivatives of three new hydrazino diacids have been prepared. They are all very readily purified by recrystallization from alcohol and uniformly contain a half atom of alkali metal in the molecule.

Conditions have been established for the preparation of benzylidene hydrazinoacetic-isobutyric acid. In contrast to most hydrazones, this substance is very soluble in water even at room temperature, which fact, coupled with the difficult solubility of the acid alkali salts, offers in part an explanation of why the alkali salts are formed exclusively on acidifying an alkaline solution of this hydrazone. The difference in the solubility of benzylidenehydrazinodiacetic acid and its alkali acid salts is not very marked, although the latter are more soluble in water than the former. Conductivity determinations carried out by Mr. W. A. Felsing, of this laboratory, show the benzylidenehydrazinodiacids to be comparatively strong electrolytes, *e. g.*, the ionization of benzylidenehydrazinodiacetic acid is about one-half that of oxalic acid.<sup>1</sup> The association of

<sup>1</sup> Conductivity determinations on benzylidenehydrazinodiacetic acid were made at 25° with the assumed ionization of only one H from the two carboxyls. The conduc-

four carboxyls in the alkali salts of three of the hydrazones of the hydrazino diacids discussed, plays no doubt an important rôle in determining their stability in the presence of mineral acids. Attention has been called to the fact that *hydroxybenzylidenehydrazinodiacetic acid*, in contrast to the simple *benzylidenehydrazone*, precipitates from an alkaline solution in the presence of a free mineral acid *only* in combination with the alkali metal. Here the acidifying influence of the OH group is self-evident.

As a further proof of the constitution of the peculiar alkali salts of the *benzylidenehydrazino diacids*, the synthesis of *hydrazinodipropionic acid* from *hydrazinomonopropionic acid* and  $\alpha$ -*bromopropionic acid* in alkaline solution was carried out. In this reaction the *hydrazinodipropionic acid* was isolated as the potassium salt of the *benzylidene derivative* and the latter proved identical with the preparation referred to above from *benzylidenehydrazinopropionic acid* and  $\alpha$ -*bromopropionic acid*. The interesting observation was made that not only is the unsymmetrical *hydrazinodipropionic acid* formed here but also the symmetrical tivity at infinite dilution used in the calculations below is taken as 457 ohms, this factor being deduced from the conductivity determinations carried out on the *monopotassium salt*.

Concentration.....	0.002 <i>M</i>	0.001	0.0005	0.0002
Conductivity.....	200.5	229.0	283.0	350.0
Ionization.....	43.86%	50.05	61.93	76.60

Conductivity determinations on the *monopotassium salt* of *benzylidenehydrazinodiacetic acid* from two stock solutions of 0.05 molar were carried out and the determinations made in duplicate showed uniformity.

Concentration....	0.05 <i>M</i>	0.02	0.01	0.005	0.002	0.001	0.0005
Conductivity....	87.8	95.1	100.1	105.7	118.7	132.4	150.1
Ionization.....	47.72%	51.40	54.10	57.15	64.15	71.60	81.20

Here the conductivity at infinite dilution was obtained by two methods: first, by plotting conductivity against concentration, which yielded the value 185; second, by the method of Noyes and Coolidge (*Carnegie Inst. Publ.*, No. 63, 50) of plotting  $1/L$  against  $(CL)^{n-1}$ . The best straight line was obtained with the  $n$  value at 1.625, yielding an  $L_\infty$  value of 188.7.

In order to determine the conductivity of the *free acid* at infinite dilution, the method was as usual:

$L_\infty$  salt —  $L_\infty K^+ + L_\infty H^+ = L_\infty$  acid, or substituting the two values of  $L_\infty$  for the potassium salt found above

$$185 - 74.8 + 347 = 457.2$$

$$188.7 - 74.8 + 347 = 460.9$$

By employing the method of Derick (*THIS JOURNAL*, 36, 2268 (1914)) for calculating the conductivity of weak acids at infinite dilution from measurements below a concentration of 0.02 *N*, the  $L_\infty$  value for *benzylidenehydrazinodiacetic acid* from the conductivity measurements at the two concentrations, 0.0005 and 0.0002 molar, was found to be 456. Of these three closely agreeing values, 456, 457.2 and 460.9, obtained by three independent methods, the number 457, as stated above, was employed in calculating the ionization of the *free benzylidenehydrazinodiacetic acid* at different concentrations.—W. A. FELSING.

isomeric diacid hydrazine, hydrazopropionic acid,  $\text{CH}_3\text{CH}(\text{COOH})\text{NH}-\text{NHCH}(\text{COOH})\text{CH}_3$ . As both hydrazinopropionic acid and benzylidenehydrazinopropionic acid are difficult to obtain, it is best to start with hydrazine hydrate, which we have found yields on treatment with  $\alpha$ -bromopropionic acid in alkaline solution the two diacid derivatives of hydrazine, hydrazinodipropionic acid and hydrazopropionic acid, and in addition hydrazinomonopropionic acid.

Above, attention has been called to the fact that Darapsky and Prabhakar interpreted the constitution of the reaction product of monobromomalonic acid on hydrazine as hydrazinodimalonic acid,  $\text{NH}_2\text{N}[\text{CH}(\text{CO}_2\text{H})_2]_2$ . They considered the possibility of this being hydrazomalonic acid but gave preference to the hydrazine formula for reasons given in the following quotation:

"Für obige Hydrazino-dimalonsäure kommen zwei Formeln in Betracht:

I.  $(\text{CO}_2\text{H})_2\text{CH} - \text{NH} - \text{NH} - \text{CH}(\text{CO}_2\text{H})_2$ . II.  $\text{NH}_2 - \text{N}[\text{CH}(\text{CO}_2\text{H})_2]_2$ .

Nach der symmetrischen Formel (I) enthält die Säure keine freie  $\text{NH}_2$ -Gruppe mehr und sollte sich darum nicht mit Benzaldehyd kondensieren. Indessen liefert auch die der asymmetrischen Formel (II) entsprechende und in analoger Weise entstehende Hydrazino-diessigsäure,  $\text{NH}_2 - \text{N}(\text{CH}_2\text{COOH})_2$ , von Curtius und Husson keine Benzalverbindung. Da ferner nach Harries und Haga auch bei der Einwirkung von Jodmethyl auf Hydrazinhydrat nur eine Amidogruppe in Reaktion tritt, und da in ähnlicher Weise nach Busch und Weiss aus Benzylchlorid und Hydrazinhydrat asymmetrisches Dibenzylhydrazin,  $\text{NH}_2\text{N}(\text{CH}_2\text{C}_6\text{H}_5)_2$  entsteht, dürfte auch obiger Hydrazinodimalonsäure die asymmetrische Formel (II) zukommen. Das schwer lösliche Bis-diammoniumsalz der Säure wäre sonach folgendermassen zu formulieren:  $2\text{N}_2\text{H}_4\text{NH}_2 - \text{N}[\text{CH}(\text{COOH})_2]_2$ ."

Attention might be called to the fact M. Busch has shown that ethyl chloroacetate reacts with phenylhydrazine to produce both symmetrical and unsymmetrical ethyl phenylhydrazinoacetate:

"Der Essigesterest vermag unter den gleichen Bedingungen sowohl an den  $\alpha$ -wie  $\beta$ -Stickstoff des Hydrazins zu treten; es entstehen beide Hydrazinoessigester neben einander, und zwar vorwiegend die asymmetrischen Verbindung." It is true, however, that free chloroacetic acid with phenylhydrazine produces "ausschliesslich die asymm.-Phenylhydrazinoessigsäure."<sup>1</sup>

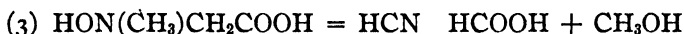
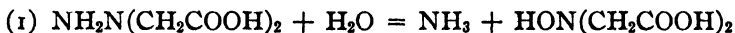
Darapsky and Prabhakar claim that hydrazinodimalonic acid will not condense with aldehydes, but do not consider this an argument against the hydrazine nature of their malonic acid derivative, because of the supposed resistance of hydrazinodiacetic acid toward condensation with aldehydes. If their substance in reality be hydrazinodimalonic acid, it is probable that in alkaline solution with benzaldehyde it will condense normally and thus furnish an affirmative proof of its constitution. The isolation of hydrazopropionic acid, although in small amount, among the reaction products of monobromopropionic acid on hydrazine or hydrazinopropionic acid, along with the observation of Busch cited above, suggests

<sup>1</sup> Ber., 36, 3878 (1903).



the possibility that some  $\alpha$ -halogen acids may be found to react with hydrazine forming exclusively hydrazo compounds.

The wide divergence between the solubility in water of hydrazinodiacetic acid and the other hydrazino diacids thus far investigated suggests the possibility of hydrazinodiacetic acid being a polymer. An attempt by Mr. W. A. Felsing in this laboratory to determine the molecular weight of hydrazinodiacetic acid in aqueous solution by the boiling-point method led to the discovery of a peculiar decomposition of this substance, which proceeds with a vigorous evolution of prussic acid and carbon dioxide, when the boiling of the solution is effected by the platinum resistance method. Another product of the decomposition is ammonia. A tentative explanation of the mechanism of the reactions involved is evident from the following equations:



In the above experiment, after boiling produces no further evolution of prussic acid and all volatile products have been removed, the solution shows a strong reducing action toward permanganate. Furthermore, if the distillate obtained from the solution be passed over a heated copper oxide spiral, a test for formaldehyde can be obtained. These facts point to the formation of formic acid and methyl alcohol rather than their equivalent, acetic acid. It is contemplated to study this peculiar behavior of hydrazinodiacetic acid quantitatively and, if possible, synthesize the assumed intermediary product, methylhydroxylaminoacetic acid.

A second plausible explanation of the processes that go on in the disruption of the hydrazinodiacetic acid molecule under the catalytic action of platinum presents itself in the assumption of oximinoacetic acid,  $\text{HON} : \text{CHCOOH}$ , as an intermediary product. Hydroxylaminodiacetic acid could pass in this oxime by the elimination of a molecule of acetic acid or the equivalent of acetic acid plus water, formic acid and methyl alcohol.



Oximinoacetic acid was discovered by C. Cramer, who reports that the substance decomposes at  $120^\circ$  into  $\text{HCN}$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$  in aqueous solution.<sup>2</sup> Hantzsch and Wild's "oximidoessigacetsäure,"  $\text{COOHCH} : \text{NOCH}_2\text{COOH}$ , undergoes a similar decomposition into  $\text{HCN}$ ,  $\text{CO}_2$ , and  $\text{HOCH}_2\text{COOH}$ .<sup>3</sup> It will be interesting to determine whether platinum

<sup>1</sup> *J. prakt. Chem.*, 83, 256 (1911); *THIS JOURNAL*, 36, 1750 (1914).

<sup>2</sup> *Ber.*, 25, 715 (1892).

<sup>3</sup> *Ann.*, 289, 301 and 302 (1896).

will exert an accelerating influence in the decomposition of these oximes similar to its catalytic action on hydrazinodiacetic acid.

If the supposed hydrazinodimalonic acid of Darapsky and Prabhakar, be in reality a hydrazine, its solubility in water, along with the observation we have made in this respect on our three hydrazino diacids, indicates that the hydrazino diacids in the aliphatic series will prove to be hygroscopic substances, difficult to obtain in a form suitable for analysis.

#### Experimental Part.

**Benzylidenehydrazinodiacetic Acid**,  $C_6H_5CH = N - N(CH_2COOH)_2$ .—Hydrazinodiacetic acid is dissolved in two mols of 2 *N* potassium hydroxide and a little less than the calculated amount of benzaldehyde added. On vigorous shaking the aldehyde disappears and on adding the calculated amount of hydrochloric acid, the benzylidene compound, mixed with its acid potassium salt, immediately separates in the form of a copious white precipitate. The hydrazone acid is very soluble in alcohol, ether, and glacial acetic acid, slightly soluble in benzene and chloroform and practically insoluble in ligroin and petroleic ether. From benzene it crystallizes sparingly in the form of long, slender prisms. For analysis it can be purified by precipitation from an ether solution with petroleic ether. On being heated, the substance begins to soften at  $115^\circ$ , turning brown, and finally melts with gas evolution at  $123^\circ$ . The hydrazone readily dissolves in hot water with hydrolysis and, on steaming off the benzaldehyde, hydrazinodiacetic acid, melting with decomposition at  $176^\circ$ , crystallizes out. The lead, barium, and calcium salts of the benzylidene compound, prepared from a solution of the diammonium salt, were found to be difficultly soluble in water but were not further investigated.

Calc. for  $C_{11}H_{12}O_4N_2$ : C, 55.93%; H, 5.08%; N, 11.86%.

Found: C, 56.28; H, 5.25; N, 11.95.

**Monopotassium Benzylidenehydrazinodiacetate**.—The monopotassium salt of hydrazinodiacetic acid, as prepared above, can be separated from the admixed free hydrazone acid by extraction of the latter with ether. The salt, recrystallized from absolute alcohol, is obtained in characteristic aggregates of microscopic needles, which decompose on heating between  $210^\circ$  and  $215^\circ$ . The same salt is obtained by treating benzylidenehydrazinodiacetic acid in alcoholic solution with one mol of potassium hydroxide, or directly from monopotassium hydrazinodiacetate in concentrated aqueous solution by treatment with the calculated amount of benzaldehyde.

Calc. for  $C_{11}H_{11}O_4N_2K$ : C, 48.18%; H, 4.01%; N, 10.22%; K, 14.23%.

Found: C, 48.24; H, 4.11; N, 10.20, 10.26; K, 14.24, 14.21.

A normal condensation of benzaldehyde with *free* hydrazinodiacetic acid can also be readily effected with a practically quantitative yield as

follows: The hydrazine is dissolved in boiling water and to the hot solution one mol of benzaldehyde, emulsified in a little water, added. The solution is now vigorously shaken with cooling under a flowing hydrant. After a few minutes the hydrazone separates, free of admixture with the original hydrazine, and can be extracted with ether. On adding petroleic ether to the ether solution, the beautifully crystallizing benzylidenehydrazinodiacetic acid separates in radiating bunches of short needles.

**Monosodium Benzylidenehydrazinodiacetate.**—If benzylidenehydrazinodiacetic acid be dissolved in a little alcohol and one mol of 2 *N* sodium hydroxide added, the liquid solidifies after a few minutes. On recrystallization from alcohol the salt is obtained in microscopic, long, slender needles, which decompose at 338°. This salt is more difficultly soluble in alcohol than the corresponding potassium salt and contains one mol of water of crystallization. The same substance is obtained by treatment of a concentrated aqueous solution of monosodium hydrazinodiacetate with the calculated amount of benzaldehyde, when the addition of alcohol at the end of the reaction effects an almost quantitative precipitation of the hydrazone salt. For analysis it was found advisable to dry the salt at 70°, as on heating to a temperature sufficiently high to expel the water of crystallization, a slight decomposition results.

Calc. for  $C_{11}H_{11}O_4N_2Na \cdot H_2O$ : C, 47.83%; H, 4.71%; N, 10.14%; Na, 8.33%.

Found: C, 47.42; H, 4.76; N, 10.23; Na, 8.22, 8.34.

**Monopotassium *o*-Hydroxybenzylidenehydrazinodiacetate.**—Free hydrazinodiacetic acid condenses with salicylaldehyde, but the reaction proceeds more slowly than it does between the hydrazine and benzaldehyde. The hydroxybenzylidenehydrazone is obtained as an oil which on standing solidifies. However, no attempt was made to prepare it in a form suitable for analysis. The condensation of hydrazinodiacetic acid with salicylaldehyde is best effected by operating with the dipotassium salt of the former: the hydrazine acid is dissolved in two mols of 2 *N* KOH, one mol of salicylaldehyde added, and the solution allowed to stand one hour for completion of the reaction. The requisite amount of standard sulfuric acid to neutralize all the potassium is then added, because, if only the calculated amount of acid to liberate the monopotassium salt be used, it effects a very incomplete precipitation. The monopotassium salt, which separates in excellent yield from the acid solution, free as far as our observation goes from any admixed hydroxybenzylidenehydrazinodiacetic acid, is best purified by recrystallization from absolute alcohol. It is thus obtained with a faint yellow tinge in microscopic needles, which decompose at 212°. This hydrazone salt contains  $\frac{1}{2}$  mol of water of crystallization. For analysis it was dried at 75°, since it is not possible to eliminate the water without the substance undergoing a slight decomposition.

Calc. for  $C_{11}H_{11}O_3N_3K \cdot \frac{1}{2} H_2O$ : C, 44.15%; H, 4.01%; N, 9.36%, K, 13.04%.

Found: C, 44.16, 44.38; H, 4.24, 4.36; N, 9.54, 9.70, 9.31; K, 12.89, 12.85, 12.77.

**The Sodium Salt of Benzylidenehydrazinoacetic-propionic Acid from the Ethyl Ester of Nitrosiminoacetic-propionic Acid.**—10.6 g. (1 mol) of monochloroacetic acid in 50 cc. of water are treated with 22.75 g. potassium carbonate (0.5 mol). After effervescence ceases, 10 g. of alanine are added, the solution boiled for three hours under a return condenser, and then evaporated to dryness. In order to isolate the reaction product, 100 cc. of methyl alcohol are poured on the residue and esterification effected by passing hydrochloric acid gas through the boiling solution. After removal of the alcohol, the residue is dissolved in a little water and a slight excess of sodium nitrite added, whereupon the nitrosamine separates as a yellow oil in good yield. The reduction of the nitroso compound is effected in 50% alcoholic solution with 3% sodium amalgam. The amalgam, 200 g. for 8 g. of the nitrosamine, is added in small amounts with cooling. Twenty-four hours are required for the completion of the reduction. The solution is then boiled for half an hour to saponify the ester, concentrated to remove the alcohol, and finally shaken out with benzaldehyde. On acidifying, a good yield of the hydrazone, 6 g. from 8 g. of the nitrosamine, is obtained. For analysis the substance was recrystallized from glacial acetic acid and then from alcohol. From either solvent it separates in the form of characteristic rectangular, thin plates as seen under the microscope, which begin to turn brown at about  $220^\circ$  and decompose completely at  $330^\circ$ .

Calc. for  $C_{14}H_{17}O_3N_4Na$ : C, 55.17%; H, 5.17%; N, 10.73%; Na, 4.41%.

Found: C, 55.18; H, 5.18; N, 10.93; Na, 4.18.

Salicylaldehyde also reacts with this hydrazine forming a hydrazone which has an alkali content similar to the benzylidene compound. Recrystallized from alcohol it melts at  $222^\circ$ .

Calc. for  $C_{14}H_{17}O_3N_4Na$ : N, 10.11%; Na, 4.15%. Found: N, 10.23; Na, 4.10.

#### Hydrochloride of Iminoacetic-propionic Acid,

$HCl.HN \begin{cases} CH_2COOH \\ CH(CH_3)COOH \end{cases}$  .—The hydrochloride of iminoacetic-propionic acid is obtained by boiling the nitroso compound, described in the above preparation, for half an hour with an excess of dilute acid under a return condenser. The solution is next evaporated to dryness, the residue dissolved in alcohol, and the salt precipitated from the alcoholic solution with ether. It melts with decomposition at  $223^\circ$ .

Calc. for  $C_5H_9O_3NCl$ : N, 7.65%. Found: N, 7.66.

**The Potassium Salt of Benzylidenehydrazinoacetic-isobutyric Acid.**—To 24.7 g. of benzylidenehydrazinoisobutyric acid in 160 cc. of water, 32 g. of potassium carbonate are added with cooling and the solution

boiled two hours under a return condenser. Upon treatment of the solution with a slight excess of acetic acid, a mixture of the unchanged benzylidenehydrazinoacetic-isobutyric acid separates out. The former is removed from the precipitate by alcohol-ether treatment and the potassium salt recrystallized from alcohol. It is thus obtained in radiating bunches of long, slender prisms, which decompose at  $209^{\circ}$ .

Calc. for  $C_{22}H_{31}O_5N_4K$ : C, 55.12%; H, 5.48%; N, 9.89%; K, 6.89%.

Found: C, 54.78; H, 5.72; N, 9.84; K, 6.60.

**Benzylidenehydrazinoacetic-isobutyric Acid**,  $C_6H_5CH = N - N(CH_2COOH)(C(CH_3)_2COOH)$ .—Two grams of benzylidenehydrazino-isobutyric acid are suspended in a little water, 2.5 g. of monochloroacetic acid and 4.5 g. of potassium carbonate added, and the solution boiled half an hour under a return condenser. In order to convert all the potassium to sulfate, 4 cc. of concentrated sulfuric acid are added and the benzaldehyde steamed off. The solution is then made alkaline with ammonia, and the dissolved hydrazino acid reconverted to the benzylidene derivatives by treatment with the calculated amount of benzaldehyde. On acidifying the solution with glacial acetic acid the benzylidenehydrazinoacetic-isobutyric acid, mixed with the ether soluble benzylidenehydrazino-isobutyric acid, separates. As benzylidenehydrazinoacetic-isobutyric acid is exceptionally soluble in water, it is necessary to operate in concentrated solution. It is very sparingly soluble in ether, chloroform, and benzene, and recrystallizes from alcohol in a matted mass of short, slender needles, which melt at  $202^{\circ}$  with decomposition. The potassium salt of benzylidenehydrazinoacetic-isobutyric acid dissolves in KOH and is reprecipitated unchanged on acidifying. On the other hand, if it be dissolved in concentrated ammonia, sulfuric acid precipitates the alkali free hydrazone just described.

Calc. for  $C_{13}H_{16}O_4N_2$ : N, 10.61%. Found: N, 10.60.

**The Potassium Salt of Benzylidenehydrazinodipropionic Acid from Hydrazinopropionic Acid or from Benzylidenehydrazinopropionic Acid.**—A mixture of one mol of hydrazinopropionic acid, one mol of  $\alpha$ -bromopropionic acid, and two mols of potassium carbonate in 10 cc. of water for every gram of the hydrazinopropionic acid used is boiled two hours under a return condenser. The solution is then treated with one mol of benzaldehyde and, after the reaction is complete, the excess of aldehyde is extracted with ether. On acidifying the solution with hydrochloric acid, a mixture of the potassium salt of benzylidenehydrazinodipropionic acid and benzylidenehydrazinopropionic acid is obtained. The separation of these two substances is described further on under the action of  $\alpha$ -bromopropionic acid on hydrazine hydrate. In the action of bromopropionic acid on hydrazinopropionic acid, there is also formed a

small amount of hydrazopropionic acid, the isolation of which may be effected through the ethyl ester by the process described later.

The potassium salt of hydrazinodipropionic acid can also be obtained by the action of  $\alpha$ -bromopropionic acid on benzylidenehydrazinopropionic acid in potassium carbonate solution by employing the method used in the preparation of the potassium salt of benzylidenehydrazinoacetic-isobutyric acid from benzylidenehydrazinoisobutyric acid, described above.

**Action of Bromopropionic Acid on Hydrazine Hydrate.**—To a solution of 20 g. (2 mols) of bromopropionic acid in 20 cc. of water, 6 g. (1 mol) of hydrazine hydrate are added slowly from a dropping funnel with cooling 18 g. of solid potassium carbonate are next added with cooling and finally the solution warmed on the water bath as long as carbon dioxide is given off. The reaction is then completed by boiling for two hours under a return condenser. The solution is now shaken out with 12 cc. of benzaldehyde, ethered out in order to remove the excess of benzaldehyde, and finally neutralized with hydrochloric acid. A yellow oil, consisting of a mixture of benzylidenehydrazinopropionic acid and the potassium salt of benzylidenehydrazinodipropionic acid, separates and solidifies on stirring. The solution is filtered and the precipitate washed with water. To obtain the potassium salt of the benzylidenehydrazinodipropionic acid free from benzylidenehydrazinopropionic acid, the latter is extracted with ether. The potassium salt is then recrystallized from absolute alcohol in the form of thin plates, melting at  $210^{\circ}$  with decomposition. The three methods of preparation of monopotassium benzylidenehydrazinodipropionate, which have been described, yield products in every way identical.

Calc. for  $C_{20}H_{31}O_8N_2K$ : C, 55.12%; H, 5.48%; N, 9.89%; K, 6.89%.

Found: C, 54.81; H, 5.89; N, 10.01; K, 6.60.

To isolate the benzylidenehydrazinopropionic acid, the ether solution obtained above is shaken out with strong potassium hydroxide and the aqueous layer neutralized with HCl. The hydrazone separates in the form of a yellow oil which solidifies on stirring. Recrystallized from benzene, the substance is obtained colorless but turns slightly yellow on exposure to air. It is soluble in all common organic solvents with the exception of petroleic ether and melts with decomposition at  $106^{\circ}$ , as described by Traube and Longinescu.<sup>1</sup>

Calc. for  $C_{10}H_{15}O_2N_2$ : N, 14.58%. Found: N, 14.50.

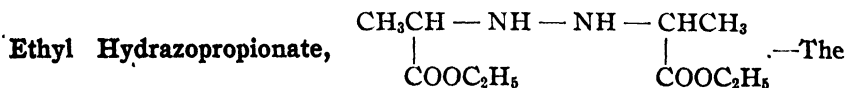
If the crude benzylidenehydrazinopropionic acid, described above, be subjected to steam distillation, it dissolves only partially while a part separates as a smear. When the solution, filtered from the smear, is

<sup>1</sup> *Ber.*, 29, 672 (1907).

concentrated on a water bath and allowed to drop slowly into alcohol, the hydrazinopropionic acid separates in the form of a white granular powder. Purified by a second precipitation from water solution with alcohol, the hydrazine melts with decomposition at  $180^{\circ}$  and agrees in all its properties with the same preparation from ethyl semicarbazinopropionate.<sup>1</sup>

Calc. for  $C_5H_8O_2N_2$ : N, 26.92%. Found: N, 26.82.

The smear referred to above solidifies on cooling. In this impure state it melts at about  $90^{\circ}$  and decomposes at approximately  $105^{\circ}$ . It is soluble in all common organic solvents but insoluble in water, alkalies, and mineral acids. All attempts to crystallize the substance failed. An analysis of the crude material gave 14.47% nitrogen.



isolation of hydrazopropionic acid in small amount among the reaction products of potassium bromopropionate on hydrazine can be effected as follows: The filtrate, obtained above from the benzylidenehydrazinomon- and dipropionic acids, is evaporated to dryness and the residue esterified according to the method of Thiele and Bailey.<sup>2</sup> In this way a substance is obtained which was carefully compared with ethyl hydrazopropionate, prepared from hydrazopropionitrile, and the two preparations were found in every respect identical. However, as this substance, especially when impure, quickly changes to an oil, it has thus far not been possible to accumulate sufficient for an analysis. Our preparation melted at  $76^{\circ}$  to a clear liquid and a mixed sample of the two preparations gave the same result. From petroleic ether both preparations separated in the form of long prisms.

**Ethyl Semicarbazinodipropionate**,  $\text{NH}_2\text{CONHN}(\text{CH}(\text{CH}_3)\text{COOC}_2\text{H}_5)_2$ . —The potassium salt of benzylidenehydrazinodipropionic acid is suspended in water, a little dilute hydrochloric acid added, and the benzaldehyde removed by steam distillation. The solution is next evaporated *in vacuo* to dryness, the residue covered with saturated alcoholic HCl and this allowed to stand twelve hours. The alcohol is then distilled off *in vacuo*, the residue taken up with a little water and the solution treated with a slight excess of KCNO with cooling. At first an oil separates, probably some of the unchanged ester, and finally the ethyl semicarbazinodipropionate crystallizes out in poor yield. The ester is soluble in hot benzene, from which it separates on cooling, more difficultly soluble in hot ether, readily soluble in alcohol and chloroform, slightly soluble in cold water, and practically insoluble in petroleic ether. After recrystallization from

<sup>1</sup> *Ann.*, 303, 85 (1898).

<sup>2</sup> *Ibid.*, 303, 87 (1898).

benzene, the substance melts at  $159^{\circ}$  with decomposition. It reduces permanganate in sulfuric acid solution, giving an oxidation product which crystallizes beautifully from alcohol. This oxidation product, while it melts at the same temperature as the expected ethyl semicarbazinopyruvate,  $\text{NH}_2\text{CO} - \text{NHN} = \text{C}(\text{CH}_3)\text{COOC}_2\text{H}_5$ ,<sup>1</sup> and has the same solubilities, differs from it in crystalline form.<sup>2</sup> Our limited supply of material did not permit a further study of this compound to determine whether a case of stereoisomerism is involved.

Calc. for  $\text{C}_{11}\text{H}_{21}\text{O}_5\text{N}_3$ : C, 48.00%; H, 7.64%; N, 15.27%.

Found: C, 48.16; H, 7.83; N, 15.56.

Bailey and Read prepared semicarbazinodiacetic acid by the action of potassium chloroacetate on semicarbazide in alkaline solution and their work suggested the possibility of employing a similar process for the preparation of semicarbazinodipropionic acid. Prolonged heating of one mol of semicarbazide and three mols of bromopropionic acid in the presence of three mols of KOH in aqueous solution at a temperature of  $60^{\circ}$  was tried.<sup>3</sup> The isolation of the reaction products was carried out by the esterification process, employed by Bailey and Read in their preparation of semicarbazinomono- and diacetic acids. However, the propionic acid rest enters only once in the semicarbazide molecule under the conditions followed above. Here the ethylsemicarbazinopropionate obtained in poor yield, gave the correct melting point and proved identical with a sample of this substance in stock.

Calc. for  $\text{C}_8\text{H}_{13}\text{O}_3\text{N}_3$ : N, 24.10%. Found: N, 23.84.

**Methylbenzylideneaminohydantoic Acid**,  $\text{C}_6\text{H}_5\text{CH} = \text{N} - \text{N}(\text{CONH}_2) - \text{CH}(\text{CH}_3)\text{COOH}$ .—Two grams of benzylidenehydrazinopropionic acid, dissolved in 10 cc. of glacial acetic acid, are treated with 1 g. of finely powdered potassium cyanate, the solution allowed to stand two hours, and then the mixture diluted with water to eight times its volume. The hydantoic acid crystallizes out slowly, colored slightly yellow. It is difficultly soluble in all common organic solvents except alcohol, from which it crystallizes in radiating bunches of short, thick, diamond-shaped crystals, melting at  $180^{\circ}$ . The substance in dilute sulfuric acid solution readily splits off benzaldehyde, yielding a beautifully crystallizing compound, which is probably 5-methyl-1-aminohydantoin.

Calc. for  $\text{C}_{11}\text{H}_{13}\text{O}_3\text{N}_3$ : C, 56.17%; H, 5.53%; N, 17.87%.

Found: C, 56.12, 56.04; H, 5.93, 5.71; N, 17.81.

<sup>1</sup> *Ann.*, 303, 87 (1898).

<sup>2</sup> See *THIS JOURNAL*, 36, 1760 (1914).

<sup>3</sup> See *Ann.*, 289, 285 (1896).



[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WASHINGTON UNIVERSITY.]

**THE NEUTRAL AMMONIUM SALTS OF SOME ORGANIC ACIDS  
AND THEIR SUBSTITUTED DERIVATIVES.**[SIXTH COMMUNICATION.<sup>1</sup>]

By LEROY MCMASTER AND A. C. MACILL.

Received May 18, 1916.

This work is a continuation of the work which has been in progress in this laboratory for several years on the preparation and investigation of the properties of the neutral ammonium salts of organic acids and their substituted derivatives. The salts previously studied were prepared by passing dry ammonia into solutions of the acids in the anhydrous solvents, methyl alcohol, ethyl alcohol, ether, acetone and benzene or in mixtures of some of these solvents. In this work we have made use of these same solvents, except methyl alcohol, and in addition we have used pure ethyl acetate. Naumann<sup>2</sup> found that a great many ammonium salts of organic acids are insoluble in ethyl acetate. Bateinan and Conrad<sup>3</sup> have recently found that the ammonium salts of some of the halogenoacetic acids are soluble in this reagent. In view of these facts, we thought it would be of interest to attempt to prepare some of the neutral ammonium salts in ethyl acetate. Several of the salts to be described were thus prepared. We have also tested the solubility of some of the ammonium salts in this solvent.

In the following work the neutral ammonium salts of tribromoacetic, phenylbromoacetic, *o*-nitrophenylacetic, phenylamidoacetic, glycolic,  $\alpha$ -bromopropionic,  $\beta$ -iodopropionic,  $\beta$ -chlorolactic, trichlorobutyric, caprylic, capric, lauric, myristic,  $\alpha$ -bromopalmitic,  $\alpha$ -bromostearic, acrylic,  $\beta$ -chlorocrotonic, erucic, dimethylmalonic, dipropylmalonic, isopropylmalonic, butylmalonic, allylmalonic, benzylmalonic, monobromosuccinic, dibromosuccinic, suberic and chlorofumaric acids have been prepared by passing dry ammonia into solutions of the respective organic acids in the above anhydrous solvents. A number of the properties of the salts were studied. The salts were quickly filtered by suction on alundum crucibles, washed with anhydrous ether, tested for neutrality, transferred to crystallizing dishes and placed for a short time in a vacuum desiccator.

The analysis of the salts consisted in determining the nitrogen by the Kjeldahl method. In all the salts except the phenylamidoacetate, the

<sup>1</sup> For previous papers on this subject see: *Am. Chem. J.*, 49, 84-7 (1913); *Chem. News*, 108, 136-7 (1913); *Am. Chem. J.*, 49, 294-301 (1913); *Chem. News*, 108, 182-3, 193-4 (1913); *THIS JOURNAL*, 36, 742-7 (1914); *Chem. News*, 110, 212-4 (1914); *THIS JOURNAL*, 36, 1916-25 (1914); *Chem. News*, 110, 224-8 (1914); *THIS JOURNAL*, 37, 2181-8 (1915); *Chem. News*, 112, 187-9 (1915).

<sup>2</sup> *Ber.*, 43, 313 (1910).

<sup>3</sup> *THIS JOURNAL*, 37, 2553 (1915).

nitrogen present as "ammonium" nitrogen was determined, which is equal to the total nitrogen, except for the phenylamidoacetate and the *o*-nitrophenylacetate. In the case of these two salts, total nitrogen was also determined.

### The Substituted Acetic Acids.

**Ammonium Tribromoacetate.**—Schäffer<sup>1</sup> has prepared and investigated the properties of many of the salts of tribromoacetic acid, but did not prepare the ammonium salt. No reference to this salt can be found in the literature. When ammonia was passed into an ether solution of the acid the salt was precipitated as glistening white leaflets, soluble in water, methyl alcohol, ethyl alcohol and ethyl acetate. It is insoluble in ether, chloroform, acetone and benzene. A solution of the salt in water is neutral. The salt is not hygroscopic, and does not give off ammonia in dry or moist air. It decomposes rapidly, with evolution of ammonia, on heating to 50° and completely volatilizes below 100°.

This salt can also be prepared by saturating an alcoholic solution of the acid with ammonia and then adding an equal volume of ether. It has the same crystalline appearance as when it is prepared in ether alone.

Calc. for  $\text{CBr}_3\text{CO}_2(\text{NH}_4)$ : 4.96%. Found: 4.96% N.

There is a close resemblance in properties between ammonium tribromoacetate and ammonium monobromoacetate prepared by Bateman and Conrad.<sup>2</sup> Both salts crystallize in white leaflets from alcohol, and are soluble in water and ethyl acetate, and insoluble in benzene. The aqueous solution of the monobromo salt slowly hydrolyzes, while the solution of the tribromo salt does not hydrolyze. Neither salt is deliquescent and both are stable in the air. Both salts decompose on warming.

**Ammonium Phenylbromoacetate.**—There is no record of this salt having been prepared, even by the method of neutralization of an aqueous solution of the acid. It can be prepared in ether or ethyl alcohol. When prepared in ether it appears as a white amorphous powder, while it is formed as a crystalline compound in ethyl alcohol. The salt is somewhat hygroscopic and is very soluble in water. The solution, which is neutral at first, rapidly hydrolyzes. It decomposes rapidly in both dry and moist air, and when heated to 50° it decomposes very quickly, ammonia being evolved. The aqueous solution on being mixed with a solution of lead acetate slowly forms a white crystalline precipitate. The neutral ammonium salt is soluble in methyl alcohol, acetic acid and an excess of ethyl alcohol. It is very slightly soluble in acetone, and insoluble in ether and benzene.

Calc. for  $\text{C}_6\text{H}_5\text{CHBrCO}_2(\text{NH}_4)$ : 6.06%. Found: 6.02% N.

**Ammonium *o*-Nitrophenylacetate.**—No reference to this salt can be

<sup>1</sup> *Ber.*, 4, 371 (1871).

<sup>2</sup> *THIS JOURNAL*, 37, 2553 (1915).

found in the literature. It readily precipitates from an ether solution in the form of pale yellow crystals. On account of its solubility in ethyl alcohol, it cannot be prepared in this medium; but if an alcoholic ammonia solution of the acid is added to a large amount of ether, the ammonium salt separates in yellow crystals. This salt was also prepared in acetone and in ethyl acetate in the form of yellow crystals. It is only very slightly soluble in these reagents, but is very soluble in water, methyl and ethyl alcohols, and acetic acid. It is insoluble in benzene and chloroform. The salt is not deliquescent and does not become acid in an aqueous solution which stood for twenty-four hours. It is stable in dry and moist air. It does not decompose at  $50^{\circ}$  but loses ammonia slowly when heated to  $100^{\circ}$ .

Both the total and the ammonium nitrogen were determined in this salt, and analyses of the salt prepared in the different solvents proved that we had the neutral salt.

Calc. for  $C_8H_9NO_2CH_2CO_2(NH_4)$ : 7.07% ammonium N. Found: 7.04% (ether); 7.03% (ethyl alc.); 7.06% (acetone); 7.02% (ethyl acetate).

Calc. for  $C_8H_{10}N_2O_4$ : 14.14% total N. Found: 14.10% (ether); 14.05% (ethyl acetate).

**Ammonium Phenylamidoacetate.**—Phenylamidoacetic acid is insoluble in ethyl alcohol, ether, benzene, ethyl acetate and acetone, but is soluble in water. While our line of work is mainly to prepare the ammonium salts in anhydrous organic solvents, nevertheless we attempted to prepare this compound in aqueous solution since the free acid is insoluble in the above reagents. Furthermore, we could find no reference to the salt having been prepared.

An aqueous solution of the acid was saturated with ammonia and the solution was allowed to evaporate to dryness. Several attempts were made to prepare the neutral salt by this method, but we obtained an acid salt in each case. This was to be expected, as most of the ammonium salts of the organic acids, when thus prepared, are the acid salts and not the neutral salts. Attention has been called to this fact in the introductory statements of the previous papers<sup>1</sup> on this work.

The neutral ammonium salt of phenylamidoacetic acid, however, was prepared by treating an alcoholic suspension of the acid with dry ammonia. Under this condition, the acid gradually passed into solution. Ether was then added to this solution and there was precipitated a salt in the form of a pale greenish gray powder. It was filtered, washed and dried in the usual way. Although the free acid is odorless, the salt thus prepared has a slight odor which is very disagreeable.

The salt is very soluble in water and benzene. It is somewhat soluble in methyl alcohol, ethyl alcohol, ethyl acetate and acetic acid. It is very

<sup>1</sup> *Loc. cit.*

slightly soluble in acetone, and insoluble in ether and chloroform. The salt can be crystallized from benzene in splendid monoclinic crystals. The aqueous solution, which is neutral at first, slowly hydrolyzes and becomes acid. The salt does not lose ammonia in dry or moist air, but it is slightly deliquescent. When warmed to  $50^{\circ}$  the salt shows no evidence of decomposition, but at  $100^{\circ}$  ammonia is given off rapidly.

Calc. for  $C_4H_5CHNH_2CO_2(NH_4)$ : 16.67%. Found: 16.62% total N.

**Ammonium Glycolate.**—Heintz<sup>1</sup> mentions the acid ammonium salt of glycolic acid and states that it crystallizes as fine needles, which are easily soluble in water and hot alcohol. Ssabanejew<sup>2</sup> describes the preparation of a neutral solution of ammonium glycolate by treating a solution of glycolic acid with the calculated amount of ammonia. The experiment was carried out in a vacuum. On evaporation of the solution, there was obtained the acid salt in needle-like crystals. The literature contains no mention of the preparation of the neutral salt by precipitation.

On passing ammonia into a dilute solution of the acid in ethyl alcohol, a white precipitate of the ammonium salt at first appeared, which soon went into solution since this salt is quite soluble in alcohol. On continuing the addition of the ammonia, heat was developed and no further precipitate formed. The alcoholic solution was allowed to evaporate in the air and there was formed a syrupy liquid and some fan-like crystals. This experiment was repeated several times. The syrupy liquid was found to distil at but a few degrees below the boiling point of pure ethyl glycolate. The liquid was evidently a mixture of the ethyl ester of glycolic acid and ammonium salts of the acid.

Results similar to this have been previously noticed by one of us<sup>3</sup> and by Bateman and Conrad.<sup>4</sup> Heat favors the formation of the esters, and attention was called to the fact in a previous paper on this subject that, when the experiments are carried out in ethyl alcohol, it is necessary to keep the flasks surrounded by cold water, for, when the ammonia is passed into the solution of the acid in alcohol, heat is set free due to the action of the ammonia on the alcohol and also to the heat of neutralization. While in most of our experiments the precipitation flasks have been kept cold when the alcohols were used as solvents for the organic acids, in this case the flask was not kept cold. No doubt that in many of the cases, where the ammonium salts of even fairly strong acids were being prepared in the alcohols and the mixtures kept cold, small amounts of esters were formed. They were removed by the excess of alcohol and by the ether used to wash the salts while in the alundum crucible.

<sup>1</sup> *Jahresb. Fortschr. Chem.*, 1861, p. 446.

<sup>2</sup> *Chem. Zentr.*, II, 32 (1899).

<sup>3</sup> McMaster, *THIS JOURNAL*, 36, 1923 (1914).

<sup>4</sup> *Loc. cit.*

However, when a very concentrated alcoholic solution of the glycolic acid was used, the precipitate, which formed at first was not redissolved and very little ester was formed. The most of the acid was converted into the ammonium salt, and the limit of the solubility of this salt in the alcohol present was reached. The salt formed in small salt-like crystals. When recrystallized from alcohol, they appeared in the form of needles.

When dry ammonia was passed into a solution of the acid in acetone, much heat was evolved and a fine white precipitate formed, which almost immediately dissolved to form a brown solution. Owing to the heat evolved, we suspected the formation of some diacetoamine by the action of ammonia on the acetone vapor present. In order to determine whether this was true, we prepared some diacetoamine by passing ammonia and acetone vapor together through a tube heated to 100°. This is the method used by Heintz<sup>1</sup> to prepare diacetoamine. To the diacetoamine was added an acetone solution of glycolic acid. Fine, white crystals were formed which were insoluble in an excess of the diacetoamine. They were presumably a salt,<sup>2</sup> formed by the action of the basic amine on the acid. If the diacetoamine is saturated with ammonia before adding the acid, white crystals form but almost immediately redissolve and form a brown solution. If some dry, neutral ammonium glycolate (preparation of which will be described later) is added to diacetoamine, it readily dissolves and forms the brown solution. From these reactions we have concluded that the white crystals which formed when the ammonia was passed into an acetone solution of the acid and which dissolved almost at once to form a brown solution, consisted of the neutral ammonium salt, soluble in the diacetoamine produced during the experiment as a result of the action of ammonia gas on the vapor of the acetone and the mixture becoming hot. While neutral ammonium salts of the organic acids have been previously prepared in acetone by one<sup>3</sup> of us, the formation of diacetoamine has not been encountered. The reason for this is probably due to the fact that the solutions were kept cool during the passing in of the ammonia, or that the heat of reaction was not so great as in this case. In fact, we repeated the experiment and kept the acetone solution of the glycolic acid cold while passing in the ammonia. No diacetoamine was formed, but it was found necessary to agitate the cold acetone solution of the acid in an atmosphere of ammonia for several hours in order to obtain a yield of the ammonium salt. The salt separated out as fine, white crystals and analysis proved it to be the neutral ammonium salt.

When ammonia was passed into a solution of the acid in benzene, coarse, large crystals formed. Analysis of these crystals showed that they

<sup>1</sup> *Ann.*, 174, 133 (1874).

<sup>2</sup> Heintz, *Ibid.*, 198, 42 (1879); 203, 336 (1880).

<sup>3</sup> McMaster.

were a mixture of the acid salt and the neutral salt. No further attempt was made to prepare the neutral salt in benzene.

The neutral ammonium salt can be easily prepared in an ethyl acetate solution of the acid. It precipitated as fine, white crystals, very soluble in water. The aqueous solution gives a neutral reaction but soon becomes acid, due to hydrolysis. The salt is also very soluble in methyl alcohol, acetic acid and diacetoamine. It is slightly soluble in ethyl alcohol and ether, and insoluble in ethyl acetate, chloroform, benzene and acetone. It decomposes slowly in dry air and very rapidly in moist air, giving off ammonia. It is also slightly hygroscopic. On warming to 50°, decomposition of the salt took place rapidly, and at 100° the salt was completely decomposed into ammonia and the acid.

Calc. for  $\text{CH}_3\text{OHCO}_2(\text{NH}_4)$ : 15.05% N. Found: 15.03% (ethyl acetate); 15.01% (acetone).

**Comparison of Results.**—The ammonium salt of phenylacetic acid has been prepared and described in a previous paper by one of us.<sup>1</sup> A comparison of the salts of phenylacetic acid and its substituted derivatives shows many points of similarity. They can all be prepared in alcohol, although phenylamidoacetic acid is insoluble in this medium. The salts of *o*-nitrophenylacetic acid and phenylamidoacetic acid are yellowish in color. The others are white. They are all soluble in water and slightly soluble in acetone, but insoluble in ether and benzene. The phenylbromoacetate and phenylamidoacetate are slightly deliquescent, while the others are not deliquescent. The phenylacetate and phenylbromoacetate give off ammonia slowly in moist air. The others do not give off ammonia in the air.

Ammonium glycolate (hydroxyacetate) is quite unlike the salts of the other substituted acetic acids. It is insoluble in acetone and slightly soluble in ethyl alcohol and ether. It is also insoluble in ethyl acetate, benzene and chloroform. It loses ammonia very rapidly in moist air. Like the phenylbromoacetate and phenylamidoacetate, it is slightly hygroscopic.

#### The Substituted Propionic Acids.

**Ammonium  $\alpha$ -Bromopropionate.**—Weinig<sup>2</sup> has investigated the properties of many of the metallic salts of  $\alpha$ -bromopropionic acid but does not mention the ammonium salt. It can be easily prepared by treating an ether solution of the acid with ammonia. The heat of reaction is so great that, in order to prevent possible decomposition of the salt, the precipitation flask must be packed in ice. The salt separates out as a noncrystalline powder. The salt is quite soluble in ethyl alcohol, and, in order to prepare it in this medium, it is necessary to saturate the alcoholic solution of the acid with ammonia and pour it into a large amount of

<sup>1</sup> McMaster, *Loc. cit.*

<sup>2</sup> *Ann.*, 280, 248 (1894).

ether. Under these conditions, the salt forms as large, flaky crystals instead of an amorphous powder, as is the case when it is prepared in the ether direct. The salt is also very soluble in methyl alcohol, acetic acid and water. The neutral aqueous solution slowly becomes acid. The salt is slightly deliquescent. It is stable in dry air but loses its ammonia slowly in a moist atmosphere. It is insoluble in ethyl acetate, chloroform, acetone and benzene. It does not decompose at  $50^{\circ}$  in dry air, but at  $100^{\circ}$  ammonia is given off slowly.

Calc. for  $\text{CH}_3\text{CHBrCO}_2(\text{NH}_4)$ : 8.23%. Found: 8.21% N (ether); 8.21% N (ethyl alcohol).

**Ammonium  $\beta$ -Iodopropionate.**—The literature contains no account of this salt. By our method it formed in ether in frost-like crystals, which gradually became amorphous. It can also be precipitated in the crystalline condition from a concentrated solution of the acid in ethyl alcohol. The salt is slightly deliquescent and readily soluble in water, forming a neutral solution which slowly becomes acid. It is quite soluble in methyl and ethyl alcohols, acetic acid and acetone, slightly soluble in chloroform, ether and ethyl acetate. It is insoluble in benzene. Upon standing several months, the salt became brown due to liberated iodine. A rancid odor also developed.

The salt does not lose ammonia in dry air, but does so very slowly in moist air. At  $50^{\circ}$  there is no evidence of ammonia being given off, but at  $100^{\circ}$  the salt decomposes slowly.

Calc. for  $\text{CH}_2\text{ICH}_2\text{CO}_2(\text{NH}_4)$ : 6.45%. Found: 6.45% N.

**Ammonium  $\beta$ -Chlorolactate.**—This salt can be prepared from a solution of the acid in either ethyl alcohol or ether. In the alcohol, the salt forms as small, white crystals and, in the ether, as a granular powder. It is not deliquescent, is stable in dry air, and readily gives off ammonia in moist air. It gives off ammonia slowly at  $50^{\circ}$  and somewhat more rapidly at  $100^{\circ}$ .

The salt is very soluble in acetic acid and water. The neutral aqueous solution soon becomes acid. Silver nitrate gives a white precipitate when added to an aqueous solution of this salt. The precipitate is soluble in ammonium hydroxide. The salt is very slightly soluble in methyl alcohol and ethyl alcohol, and insoluble in ether, chloroform, acetone, benzene and ethyl acetate. No mention of this salt can be found in the literature, although many of the other salts of  $\beta$ -chloroacetic acid have been studied.

Calc. for  $\text{CH}_2\text{ClCH}(\text{OH})\text{CO}_2(\text{NH}_4)$ : 9.89% N. Found: 9.85% (ether); 9.87% (ethyl alc.).

**Comparison of Results.**—The neutral ammonium salts of propionic acid<sup>1</sup> and its substituted derivatives, thus far studied, can be prepared

<sup>1</sup> *Am. Chem. J.*, 49, 299 (1913).

in ether from which they separate as amorphous solids. The  $\beta$ -iodopropionate and  $\beta$ -chlorolactate can be precipitated as white crystals from concentrated alcoholic solutions of the acids. The  $\beta$ -chlorolactate is slightly soluble in ethyl and methyl alcohols. The other ammonium propionates are readily soluble in these solvents. All of them are very soluble in water and acetic acid, and insoluble in benzene. They are unstable in moist air, losing ammonia rapidly. The  $\beta$ -chlorolactate is not deliquescent, while the others are.

### Some Higher Fatty Acids, Including Several Substituted Derivatives.

**Ammonium Trichlorobutyrate.**—Garzarolli-Thurnlak<sup>1</sup> prepared this salt by treating an ether solution of the acid with solid ammonium carbonate. The ether was evaporated from this mixture by means of a stream of dry air. The salt was then extracted from the residue by means of more ether. It crystallized out of water partly in tuft-like and partly in quartz-like crystals. The salt was found to be more readily soluble in water and alcohol than in ether.

We prepared this salt in ether by our usual method. It formed as a white amorphous solid. It is very soluble in ethyl alcohol, and on this account, the yield is small if the ammonia is conducted even into a saturated alcoholic solution of the acid. It can be prepared also by passing ammonia into a saturated solution of the acid in acetone or ethyl acetate and then adding a large amount of ether. In each solvent the precipitate formed was crystalline. It dissolved readily in water, the solution remaining neutral for at least several days. The salt is also very soluble in methyl alcohol and appreciably so in ethyl acetate and acetone, and very slightly soluble in chloroform and ether. It is insoluble in benzene. It is not hygroscopic.

At ordinary temperatures the salt is stable in dry air, but at 50° ammonia is rapidly given off. Ammonia is given off slowly in moist air at room temperature. When heated to 100°, the salt decomposes into the acid and ammonia.

Calc. for  $C_3H_4Cl_3CO_2(NH_4)$ : 6.73% N. Found: 6.70% (ether).

Ammonium butyrate has been described in one of the papers previously referred to. Ammonium trichlorobutyrate undergoes decomposition into ammonia and the acid salt very slowly in the air, while ammonium butyrate does so very rapidly. The aqueous solution of the latter hydrolyzes very rapidly while that of the former does so very slowly. Both the butyrate and the trichlorobutyrate are easily precipitated from ether solutions of the acids, the first one in the form of granular crystals and the second one as an amorphous powder. Both are soluble in the alcohols, acetic acid and acetone. Ammonium isobutyrate, also described

<sup>1</sup> *Ann.*, 182, 185 (1876).



in a previous paper, precipitates from an ether solution of the acid as a lustrous white solid and differs from the butyrate and the trichlorobutyrate in that it has a very high vapor tension. The ammonium butyrate is deliquescent, while the isobutyrate and the trichlorobutyrate are not deliquescent. The ammonium isobutyrate resembles the other two as to solubility in the alcohols.

**Ammonium Caprylate.**—Currie<sup>1</sup> found that he could prepare this salt by passing dry ammonia into a benzene solution of the acid. He obtained needle-like crystals, which readily hydrolyzed in an aqueous solution, and which readily gave off the odor of caprylic acid when exposed to the air. No analysis of the salt was recorded by Currie. We have prepared the salt in ether. It dried to a cheese-like mass. It did not precipitate from ethyl alcohol, but when a mixture of equal parts of ether and alcohol were used, it precipitated as monoclinic crystals. An aqueous solution of the salt lathers freely on shaking. This solution, which is neutral at first, becomes acid on standing a very short time. The salt is slightly hygroscopic, loses ammonia very slowly in dry air and very rapidly in moist air. It is very soluble in acetic acid and ethyl alcohol, and slightly soluble in methyl alcohol. It is less soluble in acetone and ethyl acetate than in methyl alcohol. It is insoluble in chloroform, ether and benzene. Analysis of the salt dried at 50° showed that there had been some decomposition.

Calc. for  $C_7H_{14}CO_2(NH_4)$ : 8.70% N. Found: 8.68% (ether); 8.64% (alcohol-ether mixt.).

After standing some weeks, the above salt became yellowish in color and developed the odor of caprylic acid.

**Ammonium Caprate.**—Currie<sup>2</sup> also describes the preparation of this salt in benzene and found that its properties are the same as those of ammonium caprylate. The salt can also be prepared in ether as a fine, white, amorphous substance, which is greasy to the touch. By conducting ammonia into a saturated alcoholic solution of the acid and then adding an excess of ether, the neutral salt precipitates as fine, white crystals. It dissolves readily in water, to which it imparts a neutral reaction. The solution quickly hydrolyzes. The salt is slightly hygroscopic. It is insoluble in benzene, slightly soluble in acetone and ether, and readily soluble in methyl alcohol, ethyl alcohol and acetic acid. It gives off ammonia slowly in dry air and rapidly in moist air. At 50° the evolution of ammonia is very rapid and is complete before the temperature reaches 100°.

Calc. for  $C_9H_{18}CO_2(NH_4)$ : 7.41% N. Found: 7.41% N.

**Ammonium Laurate.**—Many of the salts of lauric acid have been pre-

<sup>1</sup> *J. Agr. Research*, 2, 8 (1914).

<sup>2</sup> *Loc. cit.*

pared by Oudemans,<sup>1</sup> who prepared the acid ammonium salt by neutralizing an aqueous solution of the acid with ammonium hydroxide, and evaporating to crystallization.

When the dry ammonia was passed into an ether solution of the acid, there was formed a curdy, white precipitate which soon changed to one flaky in appearance. It was also prepared by adding ether to an alcoholic ammonia solution of the acid. In this case, fine, white crystals formed. The salt is very soluble in water. This aqueous solution remains neutral for at least two days. It also lathers very freely when shaken. The salt is soluble in methyl and ethyl alcohols and acetic acid, slightly soluble in acetone, and insoluble in chloroform, ether and benzene. The salt is deliquescent. It does not lose ammonia in exposure to dry or moist air. It gives off ammonia slowly at 50° and decomposes very rapidly at 100°.

Calc. for  $C_{11}H_{23}CO_2(NH_4)$ : 6.45% N. Found: 6.44% (ether); 6.43% (ether-alc. mixt.).

**Ammonium Myristate.**—No record can be found of the preparation of this salt. It can be prepared by passing dry ammonia into an ether solution of myristic acid. On passing in the gas, there was formed a fine, white, noncrystalline precipitate. By dissolving this precipitate in ethyl alcohol and evaporating the solvent, the salt was obtained in the crystalline form. It is easily soluble in water, the solution remaining neutral at the end of two days. It is readily soluble in ethyl alcohol, methyl alcohol and acetic acid, and insoluble in ether, benzene, acetone and chloroform. It is not hygroscopic. At ordinary temperatures there is no evidence of decomposition in dry air, but it decomposes slowly at 50° and is completely decomposed at the temperature of boiling water. It decomposes very slowly in moist air.

Calc. for  $C_{18}H_{37}CO_2(NH_4)$ : 5.71%. Found: 5.70% N.

**Ammonium  $\alpha$ -Bromopalmitate.**—We could find no record of the preparation of this salt. When prepared by passing ammonia into an ether solution of the acid, it precipitated first as a gelatinous mass, which soon changed to an amorphous powder. It could not be precipitated in alcohol, owing to its solubility in that solvent; but when a saturated alcoholic solution of the acid, into which ammonia had been passed for some time, was poured into a rather large volume of ether, the salt formed in fine, frost-like crystals.

The salt dissolves easily in water. The solution lathers copiously on shaking. We have here another example of an ammonium soap. This is true of the ammonium salts of all the higher fatty acids, such as capric acid, caprylic acid, myristic acid, etc. The neutral aqueous solution hydrolyzes very slowly. The salt is very soluble in acetic acid, methyl

<sup>1</sup> *Jahresb. Fortschr. Chem.*, 1863, p. 331.

alcohol and ethyl alcohol. When the ethyl alcohol solution of the salt is warmed, there is some decomposition of the salt and an ester is formed. The salt is insoluble in ether, benzene and chloroform, and slightly soluble in acetone. It loses ammonia very slowly in dry air and rapidly in moist air. It gives off but little ammonia at 50°, but decomposition takes place rapidly at 100°. The salt is not hygroscopic.

Calc. for  $C_{15}H_{31}BrCO_2(NH_4)$ : 3.99% N. Found: 3.95% (ether); 3.95% (ether-alc. mixt.).

Ammonium palmitate, described in a previous paper by McMaster,<sup>1</sup> and ammonium bromopalmitate can both be prepared in ether. The first is soluble in acetone, while the second is only slightly soluble. Both are soluble in water, methyl alcohol and ethyl alcohol. Both lather very freely in water, indicating ammonium soaps. The aqueous solution of the palmitate hydrolyzes much more rapidly than that of the bromopalmitate. The latter decomposes in the air more slowly than the first. Neither salt is hygroscopic.

**Ammonium  $\alpha$ -Bromostearate.**—As in the case of the corresponding bromopalmitate, no record of this salt can be found in the literature. It was prepared in ether as a noncrystalline compound. It was also precipitated from an alcoholic ammonia solution of the acid upon the addition of ether. In this case it formed small, white crystals. The aqueous solution lathers freely on shaking and very slowly becomes acid. The salt is not deliquescent. It is stable in dry air but loses ammonia in moist air. It is soluble in methyl and ethyl alcohols, slightly soluble in cold acetone and readily soluble in hot acetone. It does not dissolve in ether, ethyl acetate, benzene or chloroform. When treated with acetic acid,  $\alpha$ -bromostearic acid is formed. The salt decomposes slowly with the liberation of ammonia both at 50° and 100°.

Calc. for  $C_{17}H_{33}BrCO_2(NH_4)$ : 3.69%. Found: 3.66% N.

The neutral ammonium salt of  $\alpha$ -bromostearic acid can thus be prepared in ether as well as the neutral salt of stearic acid. The preparation and properties of this latter salt have been previously described by McMaster. Both salts are soluble in water, methyl alcohol, ethyl alcohol and acetone. In the last solvent the bromostearate is less soluble than the stearate. Both salts are not hygroscopic, do not lose ammonia in dry air, but do in moist air.

**Comparison of Results.**—Including those neutral-ammonium salts described in the previous papers, there have thus far been prepared and studied twenty-two salts of the saturated monobasic acids of the aliphatic series, or derivatives of acids of that series. We have found that there is a very wide variation in many of their properties. There seems to be no uniformity in their action when exposed to the air. Some of

<sup>1</sup> *Loc. cit.*

them do not deliquesce, some do so very slowly, and some very rapidly. Some of these salts lose ammonia in the air with varying degrees of rapidity, while others of them do not lose ammonia. Most of these salts hydrolyze, but not all of them. They all have the general property of being soluble in water and more or less so in the alcohols. Most of them are slightly soluble in acetone. All are insoluble in benzene and ether. A few of them have also been found to be insoluble in ethyl acetate.

#### Some Monobasic Unsaturated Acids.

**Ammonium Acrylate.**—When dry ammonia was passed into an ether solution of acrylic acid, a gelatinous mass was formed. This condition did not change when the substance was dried in an atmosphere of ammonia. This same gelatinous, glue-like mass was formed also in an alcoholic solution of the acid, even when the solution was packed in ice. We also attempted to prepare the salt in acetone. On passing in the ammonia, there was formed at first a white precipitate, which very soon redissolved and formed a light brown solution. The heat of reaction was sufficient to raise the temperature almost to the boiling point of the acetone. No doubt there was formed here again some diacetoamine in which the salt, which first formed, was redissolved. The results in this case were the same as we had in the case of the glycolic acid.

The neutral ammonium acrylate was finally prepared by passing the ammonia into a benzene solution of the acid and evaporating off the benzene. Monoclinic crystals were obtained. If a solution of the acid in ethyl acetate be used, the salt separates as a fine, granular mass. The salt, prepared in either medium, is not hygroscopic, does not lose ammonia when exposed to dry or moist air, and does not decompose when warmed to 100°. After standing several months, the salt developed the odor of acrylic acid. An aqueous solution of the salt slowly hydrolyzes.

The salt is soluble in water and acetic acid, slightly soluble in methyl and ethyl alcohols, and insoluble in ether, chloroform, ethyl acetate, acetone and benzene. No previous record of this salt could be found.

Calc. for  $\text{CH}_2\text{CHCO}_2(\text{NH}_4)$ : 15.73%. Found: 15.69% N (benzene). Prepared in ethyl acetate. Found: 15.70% N.

**Ammonium  $\beta$ -Chlorocrotonate.**—Sarnow<sup>1</sup> prepared the ammonium salt of the  $\alpha$ -acid by treating the acid with a saturated solution of ammonium carbonate. He found that the salt crystallized out from the solution in plate-like crystals, which sublimed at 100°. No mention is made of the ammonium salt of the  $\beta$ -acid.

When prepared by our method, the salt of the  $\beta$ -acid was precipitated from an ether solution as small, flaky crystals. The salt is very soluble in ethyl alcohol, but can be prepared by pouring a saturated, alcoholic ammonia solution of the acid into ether. It here separates out as a fine,

<sup>1</sup> *Ann.*, 164, 99 (1872).

white, crystalline mass. The salt was also precipitated as fine crystals in acetone.

The salt is not hygroscopic. It is very soluble in water and forms a neutral solution, which soon hydrolyzes. The salt is stable in dry air, but loses ammonia slowly in moist air. The salt is also very soluble in methyl alcohol and acetic acid as well as in ethyl alcohol. It is only slightly soluble in acetone and ethyl acetate. It is insoluble in ether, chloroform and benzene. It can be dried at  $100^{\circ}$  without decomposition.

Calc. for  $C_3H_5ClCO_2(NH_4)$ : 10.18% N. Found: 10.14% (ether); 10.19% (acetone); 10.15% (ether-alc. mixt.).

Ammonium crotonate has been described by McMaster. It was prepared, as we have prepared the  $\beta$ -chlorocrotonate, in ether and in a saturated alcoholic solution of the acid. In the case of the  $\beta$ -chlorocrotonate, it was necessary to add ether to the alcoholic ammonia solution before precipitation took place. Both salts separate from ethyl alcohol in a crystalline condition, and both are readily soluble in water. The aqueous solution in each case quickly hydrolyzes. Both salts are also soluble in methyl alcohol and acetic acid, and insoluble in chloroform and ether. Neither salt is deliquescent.

**Ammonium Erucate.**—A cream-colored, amorphous precipitate of this salt formed when ammonia was passed into the ether solution of the acid. Erucic acid is only slightly soluble in ethyl alcohol, and we thus obtained a small yield of white crystals in this solvent. The solution of the salt in water also lathers freely on shaking. The aqueous solution, neutral at first, hydrolyzes. The salt does not lose ammonia in dry air, but does so very slowly in moist air. It is not hygroscopic and can be dried at  $100^{\circ}$  without decomposition.

The salt is very slightly soluble in ethyl alcohol and somewhat more soluble in methyl alcohol. It crystallizes from the latter in monoclinic crystals. The salt is sparingly soluble in acetone and insoluble in ether, ethyl acetate and benzene. It is readily soluble in acetic acid.

Calc. for  $C_{21}H_{41}CO_2(NH_4)$ : 3.94% N. Found: 3.91% (ether); 3.95% (ethyl alc.).

The literature makes no mention of this salt so far as we can find.

**Comparison of Results.**—The neutral ammonium salts of crotonic, oleic, and elaidic acids have been described by McMaster in previous papers. With the exception of ammonium acrylate, the salts of the unsaturated monobasic acids can be prepared in ether, from which they separate in gelatinous masses, which gradually change over to amorphous solids. Ammonium oleate can be prepared in a crystalline form if ammonia is passed in for a sufficient length of time. The acrylate can be prepared in ethyl acetate. These salts are all soluble in ethyl alcohol, methyl alcohol and water. They all separate from an alcoholic solution

on evaporation as fine, white crystals. Their aqueous solutions hydrolyze. They are not deliquescent.

### The Substituted Malonic Acids.

**Ammonium Dimethylmalonate.**—There is no mention in the literature of the neutral ammonium salts of the substituted malonic acids included in this investigation. Ammonium dimethylmalonate can be prepared from a solution of the acid in ether or ethyl alcohol by our method. In ether, it is precipitated as a curdy mass, which, on washing and drying, becomes a white, amorphous powder. In alcohol, it is precipitated as crystals.

The salt forms a neutral solution in water and soon hydrolyzes. The salt is very deliquescent, and gives off ammonia slowly in dry air and very rapidly in moist air. It decomposes into ammonia and the acid when heated to 50°. The salt is readily soluble in methyl alcohol and acetic acid, slightly soluble in ethyl alcohol and ethyl acetate, and insoluble in ether, benzene, chloroform and acetone.

The neutral salt can also be prepared in ethyl acetate and acetone. From each of these solvents it readily precipitates in a crystalline form.

Calc. for  $(\text{CH}_3)_2\text{C}(\text{CO}_2\text{NH}_4)_2$ : 16.87% N. Found: 16.80% (ether); 16.79% (ethyl alc.); 16.81% (ethyl acetate); 16.85% (acetone).

**Ammonium Dipropylmalonate.**—This salt was prepared from solutions of the acid in ether, ethyl alcohol, ethyl acetate and acetone. From ether, it was precipitated as a gelatinous mass which changed to hard lumps. These lumps were crushed, washed and dried. From solutions of the acid in ethyl alcohol, ethyl acetate and acetone, the neutral salt precipitated as white, monoclinic crystals. It was necessary to surround the ethyl alcohol solution with ice to prevent the formation of an ester. The salt formed a solution in water which remained neutral for at least several days. It is slightly deliquescent. It does not give off ammonia in dry or moist air. There is no decomposition at 50°, but at 100° ammonia is slowly evolved.

The salt is readily soluble in acetic acid and methyl alcohol. It is slightly soluble in ethyl alcohol and ethyl acetate, and insoluble in ether, acetone, chloroform and benzene.

Calc. for  $(\text{C}_3\text{H}_7)_2\text{C}(\text{CO}_2\text{NH}_4)_2$ : 12.61% N. Found: 12.59% (ether); 12.58% (ethyl alc.); 12.56% (ethyl acetate); 12.62% (acetone).

**Ammonium Isopropylmalonate.**—On addition of dry ammonia to an ether solution of the acid, this salt formed as a mucilaginous precipitate which, on drying, collected in hard lumps. From ethyl alcohol, it precipitated as white crystals.

The salt is very deliquescent, and on exposure to moist air breaks up into ammonia and the acid. It is stable in dry air at ordinary tempera-

tures. At 50° it gives off ammonia slowly. At 100° the decomposition is somewhat more rapid.

An aqueous solution of the salt remains neutral to litmus. The salt is very soluble in methyl alcohol and acetic acid. It is very slightly soluble in ethyl alcohol and benzene, and insoluble in acetone, ethyl acetate and chloroform.

Calc. for  $C_5H_7CH(CO_2NH_4)_2$ : 15.55% N. Found: 15.52% (ether); 15.50% (ethyl alc.).

**Ammonium Butylmalonate.**—From a solution of the acid in ether this salt precipitated in asbestos-like fibers, which dried to a hard mass. From ethyl alcohol it precipitated as rhombic crystals. In order to prevent the formation of some ester, it was necessary to keep the alcohol solution packed in ice.

The salt is slightly deliquescent, and readily dissolves in water to form a neutral solution, which soon becomes acid to sensitive litmus. The salt is stable in dry air at room temperature, but at 50° ammonia is slowly evolved. It loses ammonia rapidly in moist air or when heated to 100°. The salt is very soluble in methyl alcohol and acetic acid, slightly soluble in ethyl acetate, and insoluble in ethyl alcohol, ether, acetone, chloroform and benzene.

Calc. for  $C_5H_9CH(CO_2NH_4)_2$ : 14.45% N. Found: 14.40% (ether); 14.40% (ethyl alc.).

**Ammonium Allylmalonate.**—Dry ammonia precipitated this salt as a fibrous mass from an ether solution of the acid. On drying this precipitate it formed as hard lumps. It formed as a white, crystalline compound of an ethyl alcohol solution of the acid. The heat of neutralization in the ethyl alcohol was sufficient to form some ester unless the solution was packed in ice. The salt was also prepared in acetone. The crystals resembled those formed in the alcohol.

The salt is very deliquescent, and loses ammonia rapidly in both dry and moist air. It is difficult to prevent decomposition of the salt, even during the drying of it. It decomposes very rapidly at 50°, and before 100° is reached, the salt loses all its ammonia.

The aqueous solution of the salt, which is at first neutral, hydrolyzes on standing. The salt is readily soluble in methyl alcohol and acetic acid, very slightly soluble in ethyl alcohol, ethyl acetate and acetone, and insoluble in chloroform, ether and benzene.

Calc. for  $C_5H_7CH(CO_2NH_4)_2$ : 15.73% N. Found: 15.74% (ether); 15.70% (ethyl alc.); 15.70% (acetone).

**Ammonium Benzylmalonate.**—This salt readily precipitated in a non-crystalline condition from a solution of the acid in ether. It precipitated as hexagonal crystals from a solution of the acid in ethyl alcohol. Neither the crystalline nor the noncrystalline form was hygroscopic.

The salt does not lose ammonia in dry or moist air even at 50°, but an

analysis of a sample kept at  $100^{\circ}$  for ten minutes showed that some decomposition had taken place. The salt dissolved readily in water, to which it imparted a neutral reaction. This solution remained neutral at least twenty-four hours. The salt is also very soluble in acetic acid and methyl alcohol, but only sparingly so in ethyl alcohol, ethyl acetate and chloroform. It is insoluble in ether, acetone and benzene.

Calc. for  $C_4H_5CH(CO_2NH_4)_2$ : 13.08% N. Found: 13.05% (ether); 13.04% (ethyl alc.).

**Comparison of Results.**—Previous papers by one of us<sup>1</sup> have given an account of the preparation and properties of the neutral ammonium salts of malonic acid and ethyl malonic acid. We have just described the neutral ammonium salts of six other substituted derivatives of malonic acid. All of these salts precipitate in ether as amorphous compounds, and as fine, white crystals in ethyl alcohol. They are all very soluble in water and insoluble in ether and benzene. With the exception of the allyl compound, all are insoluble in acetone. Most of them lose ammonia in moist air. The aqueous solutions of the salts of dimethyl, butyl and allylmalonic acids hydrolyze. The aqueous solutions of the others do not hydrolyze. The salts of malonic and benzylmalonic acids do not deliquesce, while all the others do. The most striking characteristics common to all these malonates is their solubility in the common alcohols. All of them are soluble in methyl alcohol and, with the exception of the butylmalonate, all are only very slightly soluble in ethyl alcohol. The butylmalonate is insoluble in this solvent.

#### The Substituted Succinic Acids.

**Ammonium Monobromosuccinate.**—Meyer and Jacobson state, in their *Lehrbuch der Organischen Chemie*, that when monobromosuccinic acid is treated with a methyl alcohol solution of ammonia the  $\beta$ -monoamide of malic acid results. The exact conditions are not given. No mention is made of the neutral ammonium salt.

When an ether solution of the acid was treated with dry ammonia, a fibrous precipitate formed which soon changed to an amorphous powder. When an alcoholic solution of the acid was used, a crystalline precipitate formed. The salt was found to be not deliquescent, and stable in moist as well as in dry air. The salt did not decompose when heated to  $50^{\circ}$ , but at  $100^{\circ}$  there was a slight decomposition.

The salt is very soluble in water and acetic acid. The aqueous solution remained neutral for several days. The salt is slightly soluble in ethyl alcohol and much less so in methyl alcohol. It is also very sparingly soluble in ethyl acetate and chloroform, and insoluble in ether, acetone and benzene. An aqueous solution of the salt gave with silver nitrate solution a white precipitate, insoluble in dilute nitric acid. With ferric

<sup>1</sup> McMaster, *Loc. cit.*



chloride solution, a yellowish brown precipitate formed, but with lead acetate solution no precipitate was formed.

Calc. for  $C_2H_2Br(CO_2NH_4)_2$ : 12.12% N. Found: 12.12% (ether); 12.10% (ethyl alc.).

**Ammonium Dibromosuccinate.**—Kekulé<sup>1</sup> prepared ammonium dibromosuccinate from an aqueous solution of the acid and found that it crystallized out of water without water of crystallization.

When ammonia was passed into an ethyl alcohol solution of the acid, the neutral salt formed as a fine, white, granular precipitate. In an ether solution, the salt first formed as a gelatinous mass, which changed to a crystalline powder. The salt is not hygroscopic. A solution of the salt in water is neutral at first but becomes slowly acid on standing. The aqueous solution gave with silver nitrate solution a white precipitate, soluble in dilute nitric acid. It also gave a yellowish brown precipitate with ferric chloride solution.

The salt is somewhat soluble in methyl alcohol. It is less soluble in ethyl alcohol than in methyl alcohol. It is soluble in acetic acid, and insoluble in ether, chloroform, ethyl acetate, acetone and benzene. The salt is stable in dry air but loses ammonia in moist air. It decomposes slowly with the evolution of ammonia at 50°. At 100° there is a rapid decomposition.

Calc. for  $C_2H_2Br_2(CO_2NH_4)_2$ : 9.03% N. Found: 9.00% (ether).

**Comparison of Results.**—Ammonium succinate has been described by McMaster. The neutral ammonium salts of succinic acid and its substituted bromo derivatives can be prepared in an ether or ethyl alcohol solution of the acids. In ether, the salts separate in an amorphous condition, and in ethyl alcohol in a crystalline form. All of them are easily soluble in water. The aqueous solution of the ammonium dibromosuccinate hydrolyzes very slowly. All of the salts described are only slightly soluble in ethyl alcohol. The salts of the bromo derivatives are insoluble in acetone, ether and benzene. All three salts are stable in dry air, and none of them deliquesce.

### Suberic Acid.

**Ammonium Suberate.**—Gantter and Hell<sup>2</sup> prepared the neutral ammonium salt of suberic acid by evaporating an ammoniacal solution of the acid in an atmosphere of ammonia and over potassium hydroxide. They obtained the salt in well-defined leaflets, which completely decomposed at 110° into ammonia and the acid.

The salt could not be prepared in ether on account of the insolubility of the acid in that medium. When dry ammonia was passed into an ethyl alcohol solution of the acid, no precipitate formed. Ether was then added to this alcoholic ammonia solution of the acid, whereupon fine,

<sup>1</sup> *Ann. Spl.*, 1, 354 (1862).

<sup>2</sup> *Ber.*, 13, 1166 (1880).

white crystals of neutral ammonium suberate formed. A white, crystalline precipitate of the salt also formed immediately when the ammonia was passed into an ethyl acetate solution of the acid.

The salt is soluble in water and methyl alcohol, slightly soluble in acetic acid, ethyl alcohol and benzene, and insoluble in acetone, chloroform and ethyl acetate. The aqueous solution of the salt does not hydrolyze.

The salt is not hygroscopic. At ordinary temperatures it does not lose ammonia in dry or moist air. At 50° it loses ammonia slowly, and at 100° the decomposition is very rapid. At 100° all the ammonia has been liberated and analysis shows that only the acid remains.

Calc. for  $C_8H_{12}(CO_2NH_4)_2$ : 13.46% N. Found: 13.40% (ether-alc. mixt.); 13.46% (ethyl acetate); 13.44% (benzene).

### Comparison of the Ammonium Salts of the Saturated Dibasic Acids.—

We have described in this and previous papers the preparation and properties of the neutral ammonium salts of sixteen saturated dibasic acids, or substituted derivatives of them, not including the hydroxy derivatives. While there is a rather wide variation in their general properties, they have many points of similarity. All of them can be prepared in ether, and in every case they separate as amorphous compounds. With the exception of ammonium pimelate, all of them readily precipitate in a crystalline condition from an alcoholic solution of the acid. In those salts having both carboxyl groups attached to the same carbon atom there appears to be a strong tendency to deliquesce. With the exception of the pimelate, those salts, which have the carboxyl groups attached to different carbon atoms, do not deliquesce. The aqueous solutions of the salts of the dibasic acids either do not hydrolyze at all or hydrolyze only very slowly. None of them give off ammonia in dry air, except the pimelate. Some of them give off ammonia very slowly in moist air. Unlike the salts of the saturated monobasic acids, all of them, except the pimelate, are only very slightly soluble in ethyl alcohol. The ammonium pimelate thus has different properties in general from the other saturated dibasic acids.

### Chlorofumaric Acid.

**Ammonium Chlorofumarate.**—Perkins<sup>1</sup> prepared this salt by allowing the acid to stand in an atmosphere of ammonia. He states that combination takes place with energy and that, if an excess of ammonia be left with the salt, there is no decomposition with removal of the chlorine. Perkins also states that, on slowly evaporating an aqueous solution of the salt, beautiful transparent crystals of the salt separate, which are moderately soluble in water and can be dried at 100° without decomposition. Mushman<sup>2</sup> found these crystals to be monoclinic.

<sup>1</sup> *J. Chem. Soc.*, 53, 699 (1888).

<sup>2</sup> *Ibid.*

By our method this salt was prepared in an ether solution of the acid. On first passing in the ammonia, a colloidal precipitate formed which passed to a gelatinous mass and then finally to a fine, white powder. In a saturated alcoholic solution of the acid, a fine, flaky, crystalline precipitate formed at once. In each case the neutral salt was formed. It is not deliquescent, and gives off ammonia very slowly in moist air. It is readily soluble in water, yielding a neutral solution which does not hydrolyze.

The salt is also soluble in acetic acid. It is very slightly soluble in methyl and ethyl alcohols, and insoluble in acetone, chloroform, ether, ethyl acetate and benzene. It can be heated to  $100^{\circ}$  without decomposition.

Calc. for  $C_2HCl(CO_2NH_4)_2$ : 15.17% N. Found: 15.14% (ether); 15.12% (ethyl alc.).

This salt has properties similar to ammonium fumarate previously prepared in this laboratory. Both salts readily precipitate from ethyl alcohol, the fumarate as an amorphous powder and the chlorofumarate as fine crystals. Both salts are very slightly soluble in ethyl alcohol, and neither salt deliquesces. Both salts are soluble in water forming neutral solutions, which do not hydrolyze.

This investigation is being continued with other organic acids and their substituted derivatives.

St. Louis, Mo.

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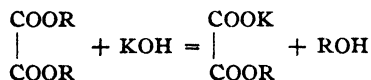
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF TORONTO.]

## THE ACTION OF A SOLUTION OF POTASSIUM HYDROXIDE IN ALCOHOL ON OXALIC ESTERS.

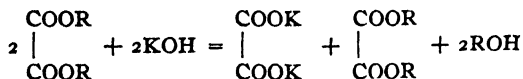
By N. C. QUA AND D. McLAREN.

Received June 15, 1916.

One method of preparing the monoalkyl esters of dibasic acids is by the treatment of the dialkyl esters with the calculated amount of the alcoholic solution of potassium or sodium hydroxide, the reaction being represented thus:



But it is clear that we might expect the results in some cases to be represented thus:



and, in other cases, the product might contain both dipotassium salt and the potassium alkyl salt.

Experiments were made with the esters of a number of dibasic acids. The ester was dissolved in the corresponding alcohol and the solution of potassium hydroxide in the same alcohol added in the proportion of a little less than one formula weight of potassium hydroxide to one formula weight of the ester. The precipitate, which usually began to appear after a few cubic centimeters of the alkali solution had been added, was filtered off, washed with the alcohol used and dried at  $100^{\circ}$ . This precipitate was analyzed by boiling with an excess of standard potassium hydroxide solution for about one and one-half hours, using a reflux condenser, and titrated back with standard acid, using phenolphthalein as indicator.

Oxalic esters gave practically pure potassium alkyl oxalate.

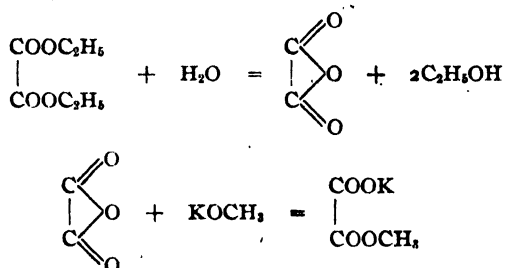
Tartaric esters gave potassium alkyl tartrate and a little dipotassium tartrate.

Succinic esters gave potassium alkyl succinate and considerable dipotassium succinate.

Phthalic esters gave dipotassium phthalate only.

Experiments with sodium hydroxide gave, in some cases, precipitates which would not crystallize and the reaction of oxalic esters with potassium hydroxide was selected for further study. It was found that for obtaining pure potassium alkyl oxalate from a dialkyl oxalate it is better not to use a very dilute solution of the ester, not to raise the temperature of the solution, and to use noticeably less than the calculated amount of potassium hydroxide.

Saloman<sup>1</sup> noticed that if ethyl oxalate be treated with a solution of potassium methylate in methyl alcohol the product was potassium methyl oxalate and he suggested representing this reaction in two stages:



Saloman's experiment was repeated, using an alcoholic solution of potassium hydroxide. Ten grams of diethyl oxalate were dissolved in 50 cc. methyl alcohol and 89 cc. of 0.767 *N* potassium hydroxide solution (in methyl alcohol) added, drop by drop, with constant shaking, the temperature being kept about  $0^{\circ}$ . This was the only case where it was found necessary to work below room temperature. The precipitate was washed with 50 cc. methyl alcohol, dried, and titrated as shown above. The re-

<sup>1</sup> *Ber.*, 8, 1509 (1875).

sult of the titration showed the precipitate to be potassium methyl oxalate. Solutions of potassium hydroxide in other alcohols were used with diethyl oxalate and also with other oxalic esters and the results are given in Table I.

TABLE I.—EFFECT OF KOH ON OXALIC ESTERS.

Diethyl oxalate.		Dimethyl oxalate.		Diisooamyl oxalate.	
Solvent alcohol.	Result.	Solvent alcohol.	Result.	Solvent alcohol.	Result.
Methyl	K methyl oxalate	Ethyl	K ethyl oxalate	Methyl	K methyl oxalate
Propyl	K propyl oxalate	Propyl	K propyl oxalate	Ethyl	K ethyl oxalate
Isoamyl	K isoamyl oxalate	Isobutyl	K isobutyl oxalate	Propyl	K propyl oxalate
		Isoamyl	K isoamyl oxalate	Isobutyl	K isobutyl oxalate

In every case the oxalic ester when treated with slightly less than the calculated amount of potassium hydroxide in alcoholic solution gave a practically pure potassium alkyl salt in which the alkyl corresponded to the alcohol used as solvent. Further experiments showed that if mixed alcohols were used as solvent the product consisted of the two potassium alkyl salts corresponding to the alcohols used.

(a) Dimethyl oxalate with potassium hydroxide in a solvent consisting of ethyl alcohol and acetone in equal proportions gave potassium ethyl oxalate.

(b) Dimethyl oxalate was dissolved in ethyl alcohol and, after two hours, the alcohol was evaporated and the remaining ester was pure, unchanged dimethyl oxalate.

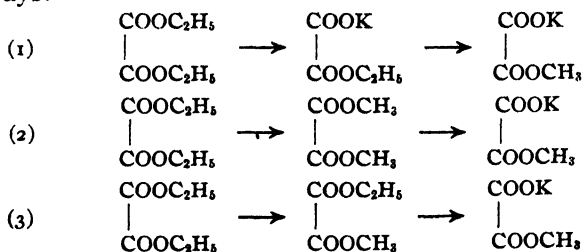
Some solubility determinations were made at room temperature with the following results:

100 cc. methyl alcohol dissolved:  
 3.0 g. potassium methyl oxalate  
 5.6 g. potassium ethyl oxalate  
 0.016 g. dipotassium oxalate

100 cc. ethyl alcohol dissolved:  
 0.15 g. potassium methyl oxalate  
 0.30 g. potassium ethyl oxalate  
 0.004 g. dipotassium oxalate

The precipitation of potassium alkyl oxalate rather than dipotassium oxalate is not due to greater insolubility of the former and, also, the precipitation of potassium ethyl oxalate rather than potassium methyl oxalate from ethyl alcohol solution is not due to greater insolubility of the potassium ethyl oxalate.

It would be possible to represent the reaction we are considering in three ways:



If either (2) or (3) is the better representation we might expect to find dimethyl oxalate or methyl ethyl oxalate in the residual dialkyl ester when considerably less than the calculated amount of potassium hydroxide solution is used.

Four cc. diethyl oxalate were dissolved in 10 cc. methyl alcohol and to this was added 2 cc. of 0.769 *N* potassium hydroxide solution in methyl alcohol but no precipitate was obtained although it was left for several hours. The alcohol was allowed to evaporate at room temperature and the dialkyl ester extracted with chloroform. The oily residue obtained by evaporation of the chloroform at room temperature might be diethyl oxalate, diethyl oxalate and dimethyl oxalate or diethyl oxalate and methyl ethyl oxalate but could not be dimethyl oxalate since the melting point of the latter is 54°. This residue was titrated and the results indicate either 7.5% dimethyl oxalate and 92.5% diethyl oxalate or 16.8% methyl ethyl oxalate and 83.2% diethyl oxalate.

Table II contains the data of a series of experiments in which varying amounts of 0.769 *N* solution of potassium hydroxide in methyl alcohol were used with 4 cc. ethyl oxalate dissolved in 10 cc. methyl alcohol. The 4 cc. ethyl oxalate used would require 38.5 cc. of the potassium hydroxide solution to completely convert it to potassium alkyl oxalate and the amount of this solution used is expressed in the first row of the table as the percentage of the total amount necessary to convert the diethyl oxalate to potassium alkyl salt. As the last three experiments in the series gave residual esters containing crystals of dimethyl oxalate the analyses of these residual esters were interpreted as indicating the proportions of dimethyl oxalate and diethyl oxalate and these appear in the last row. The analyses were done in duplicate and the average taken.

TABLE II.

Diethyl Oxalate (4 cc.) Dissolved in 10 cc. of Methyl Alcohol.

KOH sol. Me alc., %.....	5.2	10.4	15.6	20.8	26.0
Dimethyl oxalate, %.....	7.5	33.0	59.5	84.6	98.7

The results of this series of experiments show that a methyl alcohol solution of potassium hydroxide converts diethyl oxalate into dimethyl oxalate and that the amount of dimethyl oxalate formed depends on the amount of potassium hydroxide used. This reaction is accompanied by another reaction which produces potassium methyl oxalate. If, in the last experiment, a further amount of 28.5 cc. of the potassium hydroxide solution had been added there would have been complete conversion to potassium methyl oxalate and it would have been the conversion of dimethyl oxalate and not of diethyl oxalate to potassium methyl oxalate.

The two stages of the reaction are, therefore, represented as first, the change of diethyl oxalate to dimethyl oxalate and, second, the change of dimethyl oxalate to potassium methyl oxalate, see (2) above.

Since experiment (b) on page 1805 showed that an oxalic ester is not converted to a different ester by treatment with another alcohol, the change must take place under the influence of the alcoholic solution of potassium hydroxide or, possibly, the potassium alkyl salt first formed acts as a catalyzer for the reaction.

Potassium ethyl oxalate was added to ethyl oxalate dissolved in methyl alcohol and, after a few hours, the dialkyl ester was found to be unchanged diethyl oxalate.

In a solution of potassium hydroxide in methyl alcohol it may be considered that potassium hydroxide and potassium methylate are in equilibrium. Addition of water to this solution would disturb this equilibrium forming more potassium hydroxide. Hence, the addition of water to the potassium hydroxide solution would hasten or retard the formation of dimethyl oxalate depending on whether the potassium hydroxide or the potassium methylate is the determining influence in the reaction.

Table III contains the results of experiments in which the solutions of potassium hydroxide in methyl alcohol contain varying amounts of water. These solutions were made up by adding the necessary weight of water to the methyl alcohol solution of the potassium hydroxide and the methyl alcohol used for dissolving the diethyl oxalate was also diluted with water.

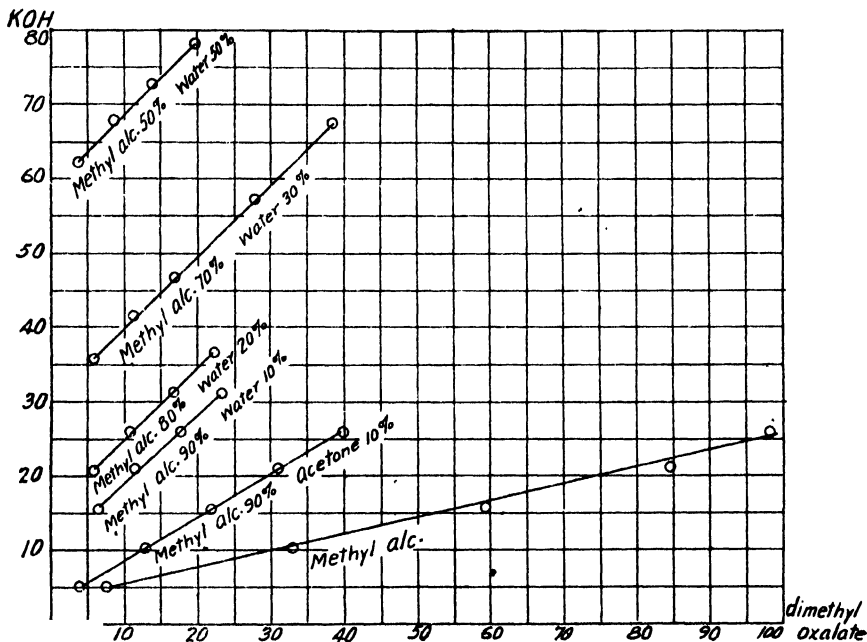
TABLE III.  
Diethyl Oxalate 4 cc. and Methyl Alcohol of Varying Strength.

10.9 cc. CH <sub>3</sub> OH (90%).		11.7 cc. CH <sub>3</sub> OH (80%).		12.9 cc. CH <sub>3</sub> OH (70%).		17.5 cc. CH <sub>3</sub> OH (50%).		11.1 cc. 90% CH <sub>3</sub> OH; 10% CH <sub>3</sub> COCH <sub>3</sub> .	
KOH sol. Me. alc. (90%). %.	Di- methyl oxalate. %.	KOH sol. Me. alc. (80%). %.	Di- methyl oxalate. %.	KOH sol. Me. alc. (70%). %.	Di- methyl oxalate. %.	KOH sol. Me. alc. (50%). %.	Di- methyl oxalate. %.	KOH sol. Me. alc. (90%). Acetone (10%). %.	Di- methyl oxalate. %.
5.2	0.0	10.4	0.0	26.0	0.0	57.2	0.0	5.2	4.0
10.4	0.0	15.6	0.0	31.2	0.0	62.4	3.9	10.4	12.9
15.6	6.5	20.8	6.0	36.4	6.0	67.8	8.75	15.6	22.0
20.8	11.5	26.0	10.9	41.6	11.5	72.8	14.0	20.8	31.1
26.0	17.9	31.2	16.9	46.8	17.0	78.0	20.0	26.0	39.9
31.2	23.5	36.4	22.6	57.2	28.0	..	..	..	..
..	..	..	..	67.6	38.5	..	..	..	..

Table III shows that under the influence of a given amount of potassium hydroxide dissolved in methyl alcohol much less dimethyl oxalate is formed when water is present and that the more water is present the less dimethyl oxalate is formed. It must be considered that the potassium methylate rather than the potassium hydroxide is the influence causing the reaction.

The last two columns which record experiments in which the alcohol was diluted with acetone instead of water shows a smaller production of dimethyl oxalate than when pure methyl alcohol was used but a much greater production than when the alcohol was diluted with the corresponding amount of water.

The results of these experiments have been represented graphically, using as one axis the amount of potassium hydroxide solution used (expressed as the percentage of the amount necessary to completely convert the diethyl oxalate to potassium methyl oxalate) and, as the other axis the percentage of dimethyl oxalate found in the residual dialkyl ester.



Saloman's representation of this reaction need not be seriously considered. It would be better to assume the formation of an addition compound of the ester with the potassium alcoholate, but, with the information at present available, it is not thought that this would help in the study of the reaction.

### Summary.

1. Dialkyl oxalates, when treated with slightly less than the calculated amount of potassium hydroxide in alcoholic solution, give a practically pure potassium alkyl oxalate in which the alkyl corresponds to the alcohol used as solvent.
2. A few solubility determinations were made which indicate that the results obtained in these experiments do not depend on the relative insolubility of the possible potassium alkyl salts.
3. If much less than the calculated amount of the methyl alcohol solution of potassium hydroxide is used with diethyl oxalate the residual dialkyl ester contains an amount of dimethyl oxalate which depends on the amount of potassium hydroxide solution used.



4. The change from diethyl oxalate to potassium methyl oxalate is represented as, first, the change of diethyl oxalate to dimethyl oxalate and, second, the change of dimethyl oxalate to potassium methyl oxalate.

5. The presence of potassium ethyl oxalate in the solution of diethyl oxalate in methyl alcohol does not cause the formation of any dimethyl oxalate.

6. If the solution of potassium hydroxide in methyl alcohol be said to contain potassium hydroxide and potassium methylate, the potassium methylate is a stronger factor than the potassium hydroxide in causing the change from diethyl oxalate to dimethyl oxalate.

These experiments were done under the direction of Professor F. B. Allan and it is proposed to continue them using solutions of other alkalies.

TORONTO, CANADA.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRESIDENCY COLLEGE.]

## HALOGENATION. XI. CHLORINATION WITH AQUA REGIA. THE CHLORINATION OF HYDROCARBONS.

BY RASIK LAL DATTA AND FRANCIS VITO FERNANDES.

Received June 17, 1916.

In continuation of the study of the chlorination of hydrocarbons by means of aqua regia,<sup>1</sup> several other hydrocarbons were subjected to its action. The results obtained were, however, mostly unsatisfactory, except in the case of a few hydrocarbons whose chloro-derivatives could be isolated by distillation or crystallization. Aqua regia has a nitrating influence on account of the nitric acid, as well as a chlorinating influence on account of the nascent chlorine. The lower hydrocarbons give only chloro-derivatives while the higher homologs usually give a mixture of both chloro- and nitro-derivatives. The reagent is quite unsuitable for chlorinating the higher hydrocarbons, while it can be successfully applied for the chlorination of the lower ones. The chlorination of the xylenes, ethyl benzene and dibenzyl gives good results; the rest of the hydrocarbons treated, either give a complicated product which cannot be separated, or break up with the formation of chloropicrin, which, as will be shown later on, is the general decomposition product under these circumstances.

### Experimental.

***m*-Xylene.**—In a typical experiment, 30 cc. of *m*-xylene were chlorinated for about six hours with 360 cc. of the mixture of HCl and HNO<sub>3</sub> (2 : 1). The mixture was heated in a flask on the wire gauze with a reflux condenser. The product was well washed with water and alkali, and kept overnight over calcium chloride.

The liquid, 25 cc., was decanted, and distilled with a stillhead. The dis-

<sup>1</sup> Datta and Fernandes, *THIS JOURNAL*, 36, 1007 (1914).

tillate was collected in two fractions, *viz.*, (1) from 140–190°, (2) from 190–224°. The volumes of the two fractions were 15.5 cc. and 9.5 cc., respectively. Thus it seemed that monochloroxylylene was formed in predominant quality, while the 4,6-dichloroxylylene was formed in slightly smaller proportion.

The two fractions were subjected to fractional distillation. After carrying out the process repeatedly, about 9 cc. of pure monochloroxylylene were obtained from the first fraction. The second fraction similarly yielded 5 cc. of pure 4,6-dichloroxylylene. These were identified in the usual manner.

The residue that was left in the distilling flask crystallized on cooling. Thin, white needles were obtained, which were pressed between the folds of filter paper and then dried in the desiccator. The melting point of the crystals was not sharp at all: it extended over a range of 15° from 195 to 210°. Thus it appeared that a mixture of chloro-derivatives was formed. Hence the solid was fractionally crystallized from hot alcohol. After the first crystallization the substance deposited from the alcoholic solution gave the m. p. 208°, although not sharp. A second crystallization gave the pure 2,4,5,6-tetrachloroxylylene with the m. p. 210°.

0.1037 gave 0.2432 AgCl; Cl = .58.01; Calc. for  $C_6Cl_4(CH_3)_2$ : Cl = 58.19.

The main portion of the substance insoluble in alcohol gave, on repeated crystallization, a small amount of trichloroxylylene, m. p. 117°. Hence the solid from the residue of distillation consisted mainly of the 2,4,5,6-tetrachloroxylylene contaminated with trichloroxylylene.

In a second experiment 25 cc. of *m*-xylene were subjected to prolonged chlorination under the conditions described above. The action was allowed to proceed for 35 hours and the mixture of acids was renewed every 5 hours, 180 cc. being used each time. After about 10 hours crystals were seen all over the liquid. The product was treated as before and kept in the vacuum desiccator. After 24 hours, it was found that crystals were deposited from the liquid. They were filtered out and drained well with suction. The liquid chloro-derivatives on distillation behaved as in the first experiment and consisted of mono- and dichloro-xylenes. The residue in the distilling flask solidified. The solid melted at about 188°. The crystals which were deposited from the liquid in vacuum also melted at about 190°. By fractional crystallization both products could be separated into the tri- and tetrachloroxylenes. The total solid product weighed 1.3 g. and on fractional crystallization gave 1.1 g. of 2,4,5,6-tetrachloroxylylene. Hence the method is specially applicable for the preparation of the tetrachloro-derivative of *m*-xylene.

***o*-Xylene.**—20 cc. of *o*-xylene were mixed with 360 cc. of the mixture of acids, and the whole heated on the wire gauze with a reflux condenser,

for about 8 hours. The product, after being separated and washed was dried in the desiccator.

The liquid deposited crystals, m. p.  $210^{\circ}$ .

The filtrate (16.5 cc.) was distilled with a stillhead and the distillate collected as follows: (1) from  $142$  to  $200^{\circ}$ , and (2) from  $200$  to  $230^{\circ}$ . The amounts of the two fractions were 11 cc. and 3.5 cc., respectively. These fractions were then distilled fractionally till they yielded products which had constant boiling points. The first gave 8.5 cc. of monochloroxylylene with the boiling point  $191.5^{\circ}$ , and the second about 1.2 cc. of 4,5-dichloroxylylene which boils at  $227^{\circ}$ .

The residue in the distilling flask solidified and the solid had the m. p.  $208^{\circ}$ . The two solids obtained must have been identical. They were crystallized from acetone, and in each case a pure solid was obtained which had the m. p.  $215^{\circ}$  and could be sublimed.

0.0917 gave 0.2177 AgCl; Cl = 58.73%. Calc. for  $C_6Cl_4(CH_3)_2$ : Cl = 58.19.

Hence the product was 3,4,5,6-tetrachloroxylylene.

***p*-Xylene.**—25 cc. of *p*-xylene were mixed with 180 cc. of the mixture of acids and heated on the wire gauze in a flask with a reflux condenser. The operation was conducted for about ten hours, the acids being renewed after five hours. The product was separated, washed and dried over calcium chloride.

In distilling the product, the maximum temperature attained was  $230^{\circ}$ . The following fractions were collected: (1)  $170$ – $200^{\circ}$ , (2)  $201$ – $230^{\circ}$ . The fractions were purified by fractional distillation; the first gave the b. p.  $186.8^{\circ}$ , and the second  $222^{\circ}$ . Thus the chloro-derivatives formed were chloroxylylene,  $C_6H_3Cl(CH_3)_2$ , and 2,5-dichloroxylylene,  $C_6H_2Cl_2(CH_3)_2$ . The quantities obtained were as follows: Volume of the whole product, 22.5 cc.; volume of chloroxylylene, 4.3 cc.; volume of 2,5-dichloroxylylene, 5 cc.

The residue in the distilling flask solidified on cooling. The solid was fractionally crystallized from hot alcohol. The pure crystals melted at  $217.5^{\circ}$ , and were soluble in ether and benzene.

0.1258 gave 0.2976 AgCl; Cl = 58.53. Calc. for  $C_6Cl_4(CH_3)_2$ : Cl = 58.19.

Thus the solid was tetrachloroxylylene. Its weight was about 0.8 g.

Hence the method is suitable for the preparation of all the derivatives mentioned above, as they are produced in fair quantities in a single operation.

In another experiment 25 cc. of *p*-xylene were treated as above for double the length of time, in order to see whether the amount of the end product had increased. There was a slight increase, but the chloroxylylene was also formed in an appreciable quantity.

**Ethyl Benzene.**—25 cc. of ethyl benzene were mixed with 360 cc. of the mixture of acids and heated on the wire gauze for about six hours.

The product was treated as usual and distilled. The temperature rose to  $206^{\circ}$ . The fraction collected between  $180$  and  $206^{\circ}$  was subjected to fractional distillation. The pure sample gave the b. p.  $201^{\circ}$ .

0.0917 gave 0.0925 AgCl; Cl = 24.95. Calc. for  $C_8H_9Cl$ : Cl = 25.26.

Hence monochloroethylbenzene,  $C_6H_5CH_2CH_2Cl$ , was formed. The quantity of this chloro-derivative was about 6 cc.

As indicated in the above investigation, the chlorine is introduced in the side-chain. To ascertain whether it was at all possible to replace the hydrogen in the nucleus, the following elaborate chlorination process was carried out: 25 cc. of the hydrocarbon were chlorinated for 37 hours, the reagent being renewed every four hours. After about 8 hours the liquid became heavy and sank beneath the acids, thus showing that the product had greater density. When the liquid was cooled a fine crop of silky white crystals was noticed, which dissolved on shaking. The crystals were formed in larger quantities at the end of the experiment.

The product was very thick in consistency. It was washed with water and alkali by decantation, the water being removed as much as possible by means of blotting paper. It was finally dried over sulfuric acid in a vacuum desiccator.

The liquid was found to have deposited crystals which had the m. p.  $160$ – $170^{\circ}$ . The little remaining liquid was subjected to distillation. The temperature rose to  $210^{\circ}$ . Thus the monochloro-derivative was formed in small quantity.

The crystals were fractionally crystallized from acetone until pure. The final product had the m. p.  $171.5^{\circ}$ . As no known chloro-derivative of ethylbenzene has this m. p. the sample is being completely investigated.

**Dibenzyl.**—The substance was treated with the mixture of acids for about four hours, the heating being done on the water bath. A brown, oily liquid was obtained, which was separated, washed with water and alkali, and dried in the vacuum desiccator. Crystals were deposited, which had the m. p.  $111^{\circ}$ . Analysis indicated the product to be pure *p*-dichlorodibenzyl,  $C_6H_4ClCH_2CH_2C_6H_4Cl$ .

0.0719 gave 0.0830 AgCl; Cl = 28.57. Calc. for  $C_6H_4ClCH_2CH_2C_6H_4Cl$ : Cl = 28.28.

**1,3,5-Butyl Xylene.**—By the chlorination of 1,3,5-butyl xylene a yellow oil was obtained from which no pure chloro-derivatives could be isolated. The smell of chloropicrin was noticed, which is a product of the action of aqua regia on several organic bodies.

Anthracene is chlorinated, to a certain extent, but the greater part of it is oxidized to anthraquinone by the nitric acid. With phenanthrene a sticky mass is obtained which does not contain any nitrogen and which is a mixture of monochlorophenanthrene and phenanthrene which could not be separated. Triphenylmethane gives a mixture of chloro-derivatives

which could not be separated. Diphenylmethane and fluorene give a mixture of chloro-derivatives, respectively, which could not be separated and isolated and in these cases no nitration takes place. In the case of naphthalene it has been found that no chlorination at all takes place, but the naphthalene is nitrated. Cymene, styrene and tetrahydronaphthalene are nitrated and chlorinated. Hydrocarbons which undergo decomposition under the influence of aqua regia, such as cymene, styrene, amylene, diisobutylene, triisobutylene, give chloropicrin which is generally a product of such decompositions, as will be shown later on. Cyclohexane, on account of its volatile nature, could not be chlorinated by means of aqua regia, whereas dimethylcyclohexane is simultaneously nitrated and chlorinated.

CALCUTTA, INDIA.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE PRESIDENCY COLLEGE.]

## HALOGENATION. XII. THE FORMATION OF CHLOROPICRIN AND TETRACHLOROQUINONE BY THE ACTION OF AQUA REGIA ON ORGANIC SUBSTANCES.

By RASIK LAL DATTA AND NIHAR RANJAN CHATTERJEE.

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In a previous communication<sup>1</sup> it has been shown that chloropicrin is formed by the action of aqua regia on several organic substances. It has now been found that whenever an organic compound breaks up destructively under the influence of aqua regia, chloropicrin is invariably produced. The chloropicrin formed is sometimes accompanied by very small quantities of other chloronitroderivatives of methane. In the case of certain aromatic compounds, tetrachloroquinone is formed as the end product of the action of aqua regia on them. As tetrachloroquinone itself breaks up to chloropicrin under the influence of aqua regia, the latter is also formed under such decompositions. The formation of chloropicrin has been noticed only in isolated cases by previous workers.

Stenhouse<sup>2</sup> showed that chloropicrin is formed by the distillation of nitro compounds with bleaching powder solution. Kekulé<sup>3</sup> obtained it by the distillation of alcohol with sodium chloride, potassium nitrate and sulfuric acid. Later on, he again prepared the substance by the action of strong nitric acid on chloral.<sup>4</sup> The action of the same reagent on chloroform was found to give chloropicrin.<sup>5</sup> Levy and Jedicka<sup>6</sup>

<sup>1</sup> Datta and Chatterjee, *THIS JOURNAL*, **37**, 567 (1915).

<sup>2</sup> *Ann.*, **66**, 241 (1848).

<sup>3</sup> *Ibid.*, **101**, 212 (1857).

<sup>4</sup> *Ibid.*, **106**, 144 (1858).

<sup>5</sup> Mills, *Ibid.*, **160**, 117 (1871).

<sup>6</sup> *Ann.*, **249**, 86 (1888).

showed that this can be obtained by the action of chlorine on nitranilic acid. Hofman<sup>1</sup> gave a method for the preparation of this compound by the action of bleaching powder on picric acid.

On examining the above modes of formation, it will be noticed that they fall into two classes. The first is the distillation of nitro compounds with bleaching powder and the second is the action of nitric acid on halogenated organic compounds containing at least three chlorine atoms. The first mode requires that the decomposing substance must have a nitro group, while the second requires the presence of three chlorine atoms, these representing the two kinds of groups attached to the carbon atoms in chloropicrin. But it was thought possible, that such a condition might be obviated altogether by subjecting any organic compound liable to such decomposition, to the simultaneous action of both nascent chlorine and nitro group; and this has been found possible. Such a reagent has been found to be aqua regia. From a study of a large number of cases, it has been found that when aqua regia acts upon a substance—no matter if it does not contain any chlorine or nitro group—chloropicrin is invariably produced, provided the substance has a tendency to decompose destructively. The formation of chloropicrin fails under those cases in which the substance is quite stable in the presence of aqua regia and has no tendency to decompose. In those cases in which chloropicrin is formed, the yield of chloropicrin obtained varies. In some cases a quantitative yield of chloropicrin is obtained, in others it is produced in moderate quantity and again in some a trace of it is formed.

Again, the formation of chloranil has been studied in a very limited number of cases. Chloranil is formed by leading chlorine into an alcoholic solution of chlorisatin.<sup>2</sup> It has been obtained by the action of a mixture of hydrochloric acid and potassium chlorate on aniline, phenol,<sup>3</sup> salicylic acid, nitrosalicylic acid and dinitrosalicylic acid.<sup>4</sup> It has also been obtained by the action of the same reagents on tyrosin<sup>5</sup> and on *m*-amino-benzoic acid.<sup>6</sup> By the interaction of fuming nitric acid on perchlorophenol, Merz and Weith<sup>7</sup> obtained chloranil. Beilstein and Kurbatow<sup>8</sup> obtained it from 1,2,4,5-tetrachlorobenzene. Barral<sup>9</sup> obtained chloranil from hexachlorocyclohexadion by means of fuming nitric acid. Elbs and Brunnschweiler<sup>10</sup> gave a method of its preparation from aniline, sodium

<sup>1</sup> *Ann.*, 139, 111 (1866).

<sup>2</sup> Erdmann, *Ibid.*, 48, 309 (1843).

<sup>3</sup> Hofmann, *Ibid.*, 52, 57 (1844).

<sup>4</sup> Stenhouse, *Ibid.*, 78, 4 (1851).

<sup>5</sup> Staedeler, *Ibid.*, 116, 99 (1860).

<sup>6</sup> Erlenmeyer, *Jahresb. Fortschr. Chem.*, 404 (1861).

<sup>7</sup> *Ber.*, 5, 460 (1872).

<sup>8</sup> *Ann.*, 192, 236 (1878).

<sup>9</sup> *Bull. soc. chim.*, [3] 11, 708 (1894).

<sup>10</sup> *J. prakt. Chem.*, [2] 52, 560 (1895).

dichromate and hydrochloric acid. Witt and Toechemittler<sup>1</sup> prepared chloranil by the treatment of 2 : 6-dichloro-*p*-phenylenediamine with potassium chlorate and hydrochloric acid. Chloranil is prepared by Graebe,<sup>2</sup> from *p*-phenylenediamine with potassium chlorate and hydrochloric acid and oxidizing the product by means of acid dichromate. It is manufactured on the large scale by the treatment of 2,4,6-trichlorophenol with chromic acid mixture. Bouveault<sup>3</sup> treats commercial chloranil with fuming nitric acid and potassium chlorate with the view of oxidizing the lower chloroquinones. One of us<sup>4</sup> has described reactions for the preparation of chloranil from *p*-phenylenediamine and hydroquinone by the action of aqua regia, which has been shown to be a good method for the preparation of chloranil.

It is evident from the above that chloranil has been prepared from a large number of sources and no generalization of their formation has as yet been noticed. It will be shown, from the study of a large number of cases, that the formation of chloroquinones is quite general in certain classes of compounds. By the action of aqua regia, which has a far greater oxidizing and chlorinating action than potassium chlorate and hydrochloric acid, on aromatic compounds, chloranil is very frequently formed; and as chloranil itself breaks up into chloropicrin by the action of aqua regia, this is also a general product of such reactions.

The essential condition of the formation of chloranil is that the aromatic compounds which are substituted in the *p*-positions, by particularly easily replaceable groups, yield tetrachloroquinone readily and with good yield, since the influence of side reaction is quite small in those cases. In the case of hydroxy and amino substituted products, chloranil is formed, but is accompanied by a large amount of tarry and other secondary products. In such cases the substance passes through a quinoid structure during the treatment with aqua regia. Again in those compounds which already possess simple or complex quinoid structures, chloranil is formed tolerably readily and in good yield. For instance, hydroquinone, which readily gives quinone on oxidation, yields tetrachloroquinone in almost quantitative yield by the action of aqua regia. Aniline black, which possesses a complex quinoid structure, yields chloranil easily. In the case of compounds which contain complex nuclei, such as naphthalene and anthracene derivatives, the formation of chloranil does not take place, the only effect is the formation of varying quantities of chloropicrin with considerable charring of the products. In the case of compounds which are otherwise substituted, considerable charring is the result with the formation of chloropicrin.

<sup>1</sup> *Ber.*, 36, 4390 (1903).

<sup>2</sup> *Ann.*, 263, 16 (1891).

<sup>3</sup> *Ann. chim. phys.*, [8] 13, 142 (1908).

<sup>4</sup> Datta, *THIS JOURNAL*, 36, 1011 (1914).

In a preliminary communication<sup>1</sup> the action of aqua regia on acetone, ether, ethyl, methyl and allyl alcohols, acetic and formic acids have been studied and it has been shown that an almost quantitative yield of chloropicrin is formed in the case of acetone suitable for the preparation of this substance in the laboratory. The action of aqua regia on the following substances has been further studied:

### Aliphatic Compounds.

*Propyl Alcohol.*—5 cc. of propyl alcohol are added to 25 cc. of a mixture of nitric and hydrochloric acids (1:2) and the whole is warmed on the water bath for three to four hours. At the end of the operation, a very pungent odor of chloropicrin is noticed and at the same time a small quantity of an oil separated. The whole is subjected to steam distillation, when a colorless oil distils over and collects at the bottom of the aqueous layer. This is pure chloropicrin as is identified by its boiling point which is between 112 to 113°.

0.2537 gave 0.6471 AgCl; Calc. for  $\text{CCl}_3\text{NO}_2$ : Cl = 64.02. Found: Cl = 63.10.

*Isopropyl Alcohol.*—The decomposition of isopropyl alcohol to chloropicrin is almost quantitative, since its immediate oxidation product is acetone, which has been found to give a good yield of chloropicrin. 10 cc. of isopropyl alcohol are added to 50 cc. of aqua regia, when an instantaneous vigorous reaction takes place with the separation of a large quantity of an oil. The reaction is completed by heating on the water bath. The product is distilled with steam and the oil collected, which, when dried and distilled, is found to be chloropicrin boiling at 112–113°.

0.1524 gave 0.3890 AgCl; Calc. for  $\text{CCl}_3\text{NO}_2$ : Cl = 64.02. Found: 63.24.

*Butyl Alcohol.*—10 cc. of butyl alcohol are taken in a flask and to this about 50 cc. of a mixture of nitric and hydrochloric acids (1:2) are added and the whole is warmed on the water bath with a reflux for three hours. A colorless oil begins to collect at the bottom which increases in quantity as the operation goes on. The whole was subjected to steam distillation and identified as usual to be chloropicrin boiling between 112–113°.

*Isobutyl Alcohol.*—5 cc. of isobutyl alcohol are added to 25 cc. of aqua regia. Only a slight reaction takes place in the cold, increasing somewhat on warming. After the end of the reaction no oil separates but a pungent smell of chloropicrin is produced, indicating that this compound is decomposed only partially.

*Glycerol.*—10 cc. of glycerol are taken in a flask fitted with a reflux condenser and to it 60 cc. of aqua regia are added. There is no reaction in the cold, but on warming on water bath a reaction seems to take place. The operation is continued for four hours. After the operation no oil separates, but a pungent smell of chloropicrin is noticed, which points to the fact that the chloropicrin which is formed only in small quantities is kept dissolved in dilute acids. The chloropicrin is secured by steam distillation and identified as usual.

*Cane sugar* gives a very small yield of chloropicrin on account of the fact that it is oxidized rapidly by the nitric acid to stable compounds such as oxalic acid. To 5 g. of cane sugar in a flask, 50 cc. of aqua regia are added. No reaction takes place in the cold, but on warming on the sand-bath reaction goes on with the charring of the sugar. On continuing the operation for three to four hours, the solution which smells distinctly of chloropicrin ultimately turns yellow.

*Maltose* gives only a trace of chloropicrin when 5 g. of maltose are heated on a reflux apparatus with 60 cc. of aqua regia. After the mixture is heated on the sand bath for

<sup>1</sup> *Loc. cit.*



four to five hours a pale yellow solution is left which has only a faint smell of chloropicrin.

*Grape sugar* is warmed on the sand bath when a trace of chloropicrin is formed.

*Starch* is warmed on the sand bath with aqua regia for three hours. At the end of the operation only a slight smell of chloropicrin is noticed.

*Methyl Ethyl Ketone*.—On treating methyl ethyl ketone with aqua regia on the water bath, a complete decomposition of the ketone takes place and an almost quantitative yield of chloropicrin is the result, which is identified as usual.

*Diethyl ketone* decomposes on treatment with aqua regia and a good yield of chloropicrin is obtained.

*Tartaric acid* is heated on the sand bath with aqua regia for several hours. In this case, no smell of chloropicrin could be noticed. Hence the substance is quite stable in the presence of aqua regia and does not decompose destructively.

*Chloroform*.—10 cc. of chloroform are treated with 60 cc. of aqua regia. No action takes place in the cold, but it goes on slowly as it is heated on the water bath with reflux. At the end of the operation only a slight smell of chloropicrin could be noticed.

*Chloral Hydrate*.—When 5 g. of chloral hydrate are treated with 30 cc. of aqua regia the reaction starts in the cold. The mixture is warmed on the water bath under reflux for three hours. At the end of the operation, a strong smell of chloropicrin is noticed.

*Allyl Mustard Oil*.—To 25 cc. of aqua regia, 4 cc. of allyl mustard oil are slowly added. At first no reaction takes place, but after a time a vigorous reaction ensues with the frothing up of the mixture. When the reaction has subsided, the whole is heated on the sand bath for two hours. At the end of the operation a pale yellow oil is found under the acid mixture. This is distilled in steam and the chloropicrin obtained is identified as usual.

*Carbamide* is heated under reflux with aqua regia for a good length of time. At the end only a slight smell of chloropicrin is noticed, pointing to the fact that urea is decomposed to a slight degree under the influence of aqua regia to form chloropicrin.

*Guanidine carbonate* is heated under a reflux on a sand bath with aqua regia. Only a trace of chloropicrin is formed which is recognized by its odor. It appears that the formation of stable salts hinders the decomposition of the compound to chloropicrin.

*Hexamethylenetetramine* is heated with an excess of aqua regia on the water bath for several hours. At the end of the operation, a colorless solution is obtained which smells only slightly of chloropicrin.

*Uric acid* is treated with aqua regia. At first no reaction takes place but after five minutes, bubbles of gas begin to rise, the substance going into solution gradually until it is completely dissolved. The mixture is heated on the sand bath for three to four hours. The resulting solution had a distinct smell of chloropicrin.

*Theobromine* on heating with the acid mixture yields a solution which smells slightly of chloropicrin.

*Caffeine*.—When the acid mixture is added to caffeine, a reaction takes place at once. The mixture is warmed on the sand bath for three to four hours. At the end the resulting solution smells distinctly of chloropicrin but no oil separates at the bottom. Hence the amount of chloropicrin formed is only minute.

### Aromatic Compounds.

*p-Aminophenol*.—On adding *p*-aminophenol to a mixture of nitric and hydrochloric acids, at first there is no action, but soon afterwards the action commences with frothing. The mixture is then warmed on the water bath for two hours, and at the end of the operation a sulfur yellow crystalline product is produced. In this case no tarry

product is formed. The yellow product obtained is crude chloranil which is purified by sublimation and is found to melt at  $289^{\circ}$  in a sealed capillary tube.

0.1621 gave 0.3728 AgCl; Calc. for  $C_6Cl_4O_2$ : Cl = 57.14. Found: 56.89.

The supernatant liquid smells strongly of chloropicrin. Hence chloropicrin is formed at the same time, which is isolated and identified in the usual manner.

*2,4-Diaminophenol*.—This was heated under a reflux with aqua regia for three hours. The product consists of a yellowish liquid smelling strongly of chloropicrin and at the same time, a yellowish brown semisolid product is deposited underneath. It was filtered, washed and dried. On sublimation, the mass charred and a sublimate was obtained in beautiful yellow plates, melting at  $289^{\circ}$ , which is pure chloranil. In this case the yield is very small, as a considerable portion is converted to a tarry mass with the formation of a large amount of chloropicrin.

*p-Diaminodiphenylamine*.—On treating the substance with aqua regia, at first very slight reaction takes place, which however is found to go on slowly on heating under reflux on a water bath. At the end of three hours, a brown solid substance is seen floating at the time, while the mixture smells strongly of chloropicrin. The operation is continued with a fresh quantity of aqua regia for some time. The brown product on sublimation gave a small yield of chloranil. 10 g. of the substance yielded 3 g. of tetrachloroquinone.

*Sulfanilic acid* is treated with aqua regia when it begins to dissolve slowly. The mixture is then warmed on the water bath under reflux when within an hour, a yellowish crystalline product is seen to be formed on the surface of the acid mixture, which gradually increases in quantity during the progress of the reaction. After three hours the operation is found to be complete, and the product obtained consists of beautiful yellow crystalline scales which is nearly pure chloranil. It is purified by a single sublimation. The supernatant liquid smells strongly of chloropicrin, pointing to the fact that a good quantity of sulfanilic acid is decomposed to chloropicrin.

*p-Nitrophenol*.—On heating *p*-nitrophenol with aqua regia for several hours, a sulfur yellow crystalline solid is obtained without any charring of product. The solution smells strongly of chloropicrin. On sublimation pure tetrachloroquinone is obtained melting at  $289^{\circ}$ .

*p-Hydroxybenzoic Acid*.—On heating *p*-hydroxybenzoic acid with aqua regia for several hours, a good yield of chloranil is obtained. This is unaccompanied by any tarry matter. The solution smells strongly of chloropicrin.

*p-Toluidine*.—When this is treated with aqua regia a reaction takes place at once. The mixture is warmed on the water bath when a dark oily substance is formed which deposits at the bottom. The liquid also smells strongly of chloropicrin. Upon prolonging the operation beautiful crystals are formed which are not chloroquinone. The product is under examination.

*p-Cresol* yields on prolonged treatment with aqua regia a smell of chloropicrin and a brown product is obtained which, however, does not yield any chloranil.

*Aniline*.—To aqua regia, aniline is added very gradually. At the end of the addition, a dark tarry product is seen floating on the acid mixture. The product is warmed on the water bath for six hours, during which the pungent smell of chloropicrin is noticed. As the operation is in progress the acid mixture is renewed. A brown pasty mass is obtained which yields a small quantity of tetrachloroquinone.

*Diphenylamine*.—To aqua regia, diphenylamine is gradually added when a reaction takes place, the solution turning dark blue. The product is warmed on the water bath with the renewal of the acid mixture, when a yellowish brown substance is obtained which gives a small yield of chloranil on sublimation. The mother liquid smells strongly of chloropicrin which is also formed in considerable quantity.

**2,4-Dichloroaniline.**—On treating dichloroaniline with aqua regia, a reaction takes place in the cold. It is continued on the water bath and at the end a brown crystalline product is obtained which gave a fair yield of chloranil. The yield in this case is much greater than from aniline or diphenylamine. Chloropicrin is also formed at the same time.

**Phenylhydrazine.**—Phenylhydrazine hydrochloride is added to aqua regia and heated on the water bath. A reaction takes place with the evolution of heat, at the end of which, a tarry product is formed. This on sublimation gives a small yield of chloranil. During the operation the solution has a very pungent smell of chloropicrin.

**Trichlorophenol.**—This compound is heated in a reflux with aqua regia on the water bath. In the course of an hour, the transformation into chloranil is perceptible by the change of brown color of the product to bright yellow and generally becomes complete after three hours. A good yield of chloranil is obtained unaccompanied by any tarry matter. The mother liquor smells strongly of chloropicrin, a good quantity of which is formed at the same time.

**Tribromophenol.**—On treating tribromophenol with aqua regia on the water bath it is found that the bromine is replaced by chlorine and ultimately tetrachloroquinone is the result. A good quantity of chloropicrin is also formed at the same time.

**Aniline Black.**—Aniline black on prolonged treatment gradually turns from black to yellow. At the same time a pungent smell of chloropicrin is noticed. The yellow substance on sublimation gives a good yield of tetrachloroquinone.

**Methyl orange** on treatment with aqua regia, yields beautiful yellow crystals unaccompanied by any tarry matter. This is sublimed to get pure chloranil which is formed in good yield. The yellowish brown liquid smells strongly of chloropicrin.

**Azobenzene** gives a brown product, as also an abundant quantity of chloropicrin. In this case only a trace of tetrachloroquinone could be obtained.

**m-Cresol** on similar treatment yields a brown product from which a very small quantity of chloranil could be isolated, but chloropicrin is formed abundantly.

**m-Phenylenediamine** on treatment with aqua regia first yields a deep brown oily liquid which subsequently turns into a yellow crystalline solid. The yellow crystalline substance gives a fair yield of chloranil. The mother liquid strongly smells of chloropicrin.

**m-Nitraniline** yields a brown semi-solid product which gives a small quantity of chloroanil and an abundant quantity of chloropicrin.

**o-Phenylenediamine** on prolonged treatment yields a tarry mass which does not give tetrachloroquinone. In this case, no chloropicrin is formed.

**o-Nitrophenol** on treatment with aqua regia gradually passes from a dark colored pasty mass to a brown substance and thence to a yellow crystalline product in course of three hours. This yields a fair quantity of chloranil. A good quantity of chloropicrin is also formed at the same time.

**o-Cresol.**—Unlike *m*- and *p*-cresols, *o*-cresol is found to give good quantities of chloranil and chloropicrin.

On treating *o*-cresol with aqua regia, a dark oily product is formed which is converted into a brown crystalline substance as the action is prolonged. This on sublimation gives chloranil. The mother liquor smells strongly of chloropicrin.

**Benzidine.**—With aqua regia, it yields a brown tarry solid which does not give any tetrachloroquinone. But in this case, a good quantity of chloropicrin is formed.

**Benzenesulfonic Acid.**—In this case no chloranil is formed but a good quantity of chloropicrin is formed.

**Benzamide.**—By the action of aqua regia on benzamide, no chloranil is formed but a yellowish white substance is formed which is under examination. In this case no chloropicrin is formed.

*Acetophenone* yields only chloropicrin and no tetrachloroquinone.

*Benzophenone* yields only chloropicrin and no chloranil. An oily substance is formed which seems to decompose to chloropicrin and no sign of the formation of a solid could be noticed.

*Resorcinol*.—By prolonged treatment of resorcinol with aqua regia as usual, a good quantity of chloropicrin is produced and also a black pasty mass, which gradually diminishes in quantity as the reaction is continued being ultimately converted into chloropicrin. In this case no chloranil is formed.

*Pyrogallic acid* yields a good quantity of chloropicrin and a colorless crystalline product which is under investigation.

*Tannic and Gallic Acids*.—The yield of chloropicrin from tannic and gallic acids is considerable. No chloranil is formed in these cases. Compounds which have got many hydroxy groups generally break up destructively with the formation of chloropicrin.

*Saccharine*.—This gives only a slight smell of chloropicrin. It, however, gives no chloranil.

*Pyridine* does not give either chloranil or chloropicrin when treated with aqua regia with which it forms salts.

*Quinoline*, however, is found to give chloropicrin in a slight degree. When heated with aqua regia, showing that the reagent decomposes the quinoline ring only partially.

*Alpha naphthol*.—This substance yields a tarry product from which only a minute quantity of tetrachloroquinone could be obtained. An abundant quantity of chloropicrin is formed.

*Beta naphthol*.—In the case of  $\beta$ -naphthol, a black substance is formed and an abundant quantity of chloropicrin. From the black substance no chloranil could be obtained. The only effect of prolonged action is that the black substance is diminished with the formation of chloropicrin.

Mesitylene, cymene and styrolene all yield chloropicrin with the charring of products. Naphthalene and anthracene yield small quantities of chloropicrin.

### The Preparation of Chloranil.

The preparation of chloranil by the action of aqua regia on hydroquinone and *p*-phenylenediamine has been described in a previous communication and it may be pointed out that they give the best yield of chloranil of any of the substances which have been treated with aqua regia. In fact this would form the best method for the preparation of chloranil on a commercial scale. The existing method of the manufacture of chloranil is the oxidation of trichlorophenol with potassium dichromate. It has been found that the yield could be increased and the product obtained purer by treating trichlorophenol with aqua regia. The next method of importance giving a good yield of chloranil is the treatment of sulfanilic acid with aqua regia. Sulfanilic acid which has amino and sulfonic groups in the *p*-positions is readily converted into chloranil, the sulfonic and amino groups being detached. The yield in this case is not so high as in the previous cases as in a good portion the molecule is ruptured with the formation of chloropicrin. In view of the fact that it is a cheap substance, this would serve as the most economical method of manufacture of chloranil on the large scale. The yields which have been obtained are as follows:

From 20 g. of hydroquinone and also of *p*-phenylenediamine 13 to 14 g. of pure chloranil could be obtained; from 20 g. trichlorophenol, a yield of 10 g. could be realized and from 20 g. of sulfanilic acid, a yield of 6-7 g. could be secured.

CALCUTTA, INDIA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF BRYN MAWR COLLEGE.]

## THE REVERSIBLE REPLACEMENT OF ALCOHOLS IN ALDEHYDEALCOHOLATES.<sup>1</sup>

BY MARGUERITE WILLCOX AND ROGER F. BRUNEL.

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### I. Introduction.

Few systematic attempts have as yet been made to study the variation of the equilibrium in reactions of organic compounds with alteration of the constitution of one of the reacting substances. Such an investigation has been undertaken here with the hope of gaining a more definite knowledge of the relation existing between the structure of aliphatic compounds and their chemical affinity, and of determining what factors play an important part in governing this relationship.

Ostwald<sup>2</sup> believed that the dissociation constants of acids, bases, and salts were determined by the constitution and composition of the substance, and could be considered as a measure of chemical affinity. He investigated the dissociation constants of organic acids at some length; but the relation between the affinity of organic acids, as expressed by their dissociation constants in solution, and their affinity, as exhibited in organic reactions, is by no means clear. In particular such attempts as that of Derick<sup>3</sup> to explain the reactions of all sorts of organic compounds by a consideration of ionization constants cannot be regarded as convincing.

Davis<sup>4</sup> has recently investigated the effect of constitution on chemical affinity by studying the equilibria reached in the hydrolysis of various substituted formamides into amines and formic acid. Since, however, his paper deals primarily with substitution in the benzene ring, the results obtained are not directly comparable with those given in this paper.

The influence which constitution exerts upon the velocity and limit of esterification of several classes of compounds, including saturated and

<sup>1</sup> Dissertation presented by Marguerite Willcox to the Faculty of Bryn Mawr College in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

<sup>2</sup> "Outlines of General Chemistry," p. 373 (1890). This subject has been extensively discussed in the chemical literature. Michael, *J. prakt. Chem.*, N. S., 60, 333, made such data the original basis of his scale of combined influence. Among others who have discussed this subject Wegscheider is particularly to be mentioned *Mon.*, 23, 287; 26, 1265; *Z. Elektrochem.*, 18, 277, and in *THIS JOURNAL*, Derick, 32, 1333 (1910).

<sup>3</sup> *THIS JOURNAL*, 32, 1333 (1910).

<sup>4</sup> *Z. physik. Chem.*, 78, 353, 369 (1911).

unsaturated, aliphatic and aromatic alcohols and acids, was studied by Menshutkin.<sup>1</sup> Table I gives the limit of esterification reached when a limited number of primary and secondary alcohols were esterified with acetic acid and a number of acids with isobutyl alcohol.

TABLE I.

Alcohols with acetic acid.		Acids with isobutyl alcohol.	
Name.	Pct. ester.	Name.	Pct. ester.
Primary.		Primary.	
Methyl alcohol.....	69.59	Formic acid.....	64.32
Ethyl alcohol.....	66.57	Acetic acid.....	67.38
Propyl alcohol.....	66.85	Propionic acid.....	68.70
<i>n</i> -Butyl alcohol.....	67.30	<i>n</i> -Butyric acid.....	69.52
Isobutyl alcohol.....	67.38	Capronic acid.....	69.81
Octyl alcohol.....	72.34	Caprylic acid.....	70.87
Cetyl alcohol.....	80.39	Secondary.	
Secondary.		Isobutyric acid.....	69.51
Dimethylcarbinol.....	60.52	Methylethylacetic acid....	73.73
Methylisopropylcarbinol....	59.31	Tertiary.	
Ethylmethylcarbinol.....	59.28	Trimethylacetic acid.....	72.60
Diethylcarbinol.....	58.66	Dimethylethylacetic acid..	74.15
Hexylmethylcarbinol.....	62.03		

When the tertiary alcohols were esterified with acetic acid, decomposition took place and unsaturated hydrocarbons were formed; consequently the percentage of ester produced was much too low. Only two general conclusions were drawn: first, that the primary, secondary, and tertiary alcohols and acids fell in three separate groups; and second, that an increase in the molecular weight in a homologous series of primary alcohols or acids was accompanied by an increase in the amount esterified. No particular explanation was given for these facts, or for the differences in the amounts of ester formed with isomeric alcohols and acids in the same group. Unfortunately, the differences between the end points reached must, in a number of cases, be less than the experimental error; therefore, there is little opportunity to draw any conclusions regarding the influence of constitution and composition upon the amount of ester formed.

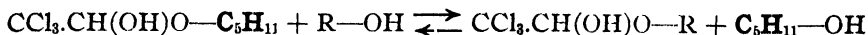
It would appear that any exact knowledge of the relation between chemical affinity, on the one hand, and constitution and composition, on the other, must be based on the investigation of reversible reactions between comparatively simple compounds in which the constitution of but one of the substances is allowed to alter. In this way the effect of changes in constitution on the equilibrium point of the reaction can be clearly traced. With this end in view, the further investigation of a reaction studied by Gadamer<sup>2</sup> and Kuntze,<sup>3</sup> the course of which can be followed

<sup>1</sup> *Ann. chim. phys.*, [5] 20, 289; 23, 14; 30, 81 (1889).

<sup>2</sup> *Arch. pharm.*, 243, 12 (1905).

<sup>3</sup> *Ibid.*, 246, 91 (1908).

polarimetrically, was undertaken. When chloral-*l*-amylalcoholate is treated with any aliphatic alcohol a reaction takes place according to the following equation:



Kuntze carried out two series of experiments with eight inactive alcohols and reached practically the same end point from whichever side of the reaction he started, from which it is evident that a true equilibrium was attained. He measured the rotation of the pure active alcoholate and alcohol in the solvent used and assumed that a linear relation existed between all intermediate values of rotations and percentages of active constituents present. This relationship he made use of in following the velocity and in measuring the end point reached in all the reactions. Proof will be given later that this assumption of a linear relationship was not correct. Since some of his readings were taken two minutes after the constituents were mixed, it seems probable that in preparing the solutions so quickly, accuracy was in some instances sacrificed; consequently no attempt has been made in this work to measure the reaction velocity, an effort being made, rather, to determine the end point of the reaction as accurately as possible. Kuntze<sup>1</sup> has more recently calculated velocity constants for four of these reactions.

## II. Method and Procedure.

In this investigation two series of experiments were carried out, in which chloral-*l*-amylalcoholate and butylchloral-*d*-sec.-butylalcoholate, respectively, were treated with twenty-two inactive alcohols. The reactions are as follows, the optically active radicals being indicated by heavy type:  $\text{CCl}_3.\text{CH}(\text{OH})\text{O}-\text{C}_5\text{H}_{11} + \text{R}-\text{OH} \rightleftharpoons \text{CCl}_3.\text{CH}(\text{OH})\text{O}-\text{R} + \text{C}_5\text{H}_{11}-\text{OH}$ , and



The determinations were carried out in benzene solution at 25°. In every case 0.025 mol of active alcoholate and an equivalent amount of inactive alcohol were accurately weighed into a measuring flask and diluted to 20 cc. The measurements were all taken in a 2-dm. jacketed polarimeter tube, maintained at 25° by a current of water from the thermostat. The polarimeter<sup>2</sup> was a Landolt-Lippich instrument with a half-shade field and with direct vision spectroscope. The source of light was a lime candle heated by an oxy-illuminating gas flame, light corresponding approximately to the sodium D lines being used. The rotations of the solutions could be read to 0.005°. In the series carried out with chloral-*l*-amylalcoholate, duplicates of all but two of the determinations were

<sup>1</sup> Z. *Electrochem.*, 18, 1015 (1912).

<sup>2</sup> No. 58 in the Schmidt and Haensch catalog.

made, which were identical in most cases and never varied by more than  $0.01^\circ$ . In the butylchloral-*d*-sec.butylalcoholate series duplicates of many of the determinations were made, but since the *d*-sec.butyl alcohol is difficult to obtain in large quantities, only one determination was made with part of the alcohols.

The reactions with primary and secondary alcohols were completed within thirty or forty minutes, the rotations having become constant. The tertiary alcohols, however, reacted more slowly, constant rotations

not being obtained in some cases for nearly two hours. When ever duplicates were made one of the solutions was allowed to stand several hours or even overnight, but no further change in the rotation ever occurred.

The determination of the end point in these reactions depends upon the fact that the active alcoholates do not have the same rotations as the active alcohols from which they are formed. It will be noticed that the difference between the rotations of butylchloral-*d*-sec.butylalcoholate and *d*-sec. butyl alcohol is much greater than that between the rotations of chloral-*l*-amylalcoholate and *l*-amyl alcohol; consequently a greater degree of accuracy is afforded by the former series of reactions. For 0.025 mol, 2.2028 g., *l*-amyl alcohol in 20 cc. benzene solution,  $\alpha_D^{25} = -1.13^\circ$ ; for 0.025 mol, 5.8871 g., chloral-*l*-amylalcoholate in 20 cc. benzene

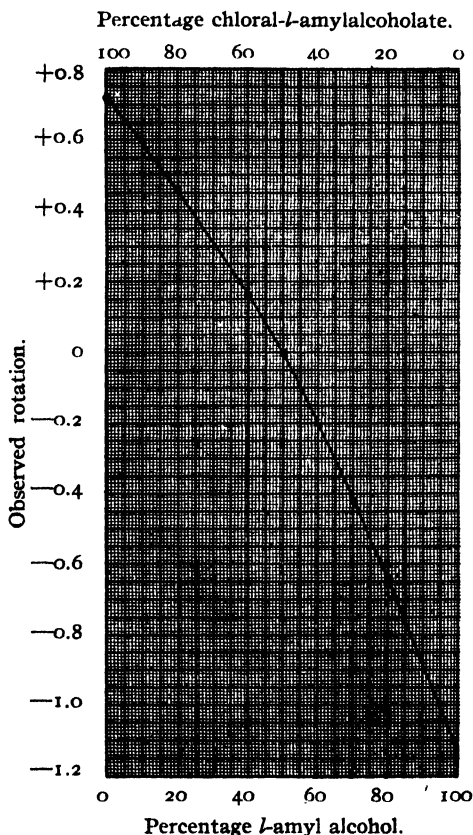


Fig. 1.

solution,  $\alpha_D^{25} = +0.72^\circ$ , the difference being  $1.85^\circ$ . For 0.025 mol, 1.8520 g., *d*-sec.butyl alcohol in 20 cc. benzene solution,  $\alpha_D^{25} = +2.60^\circ$ ; for 0.025 mol, 6.2375 g., butylchloral-*d*-sec.butylalcoholate in 20 cc. benzene solution,  $\alpha_D^{25} = +10.20^\circ$ , the difference being  $7.60^\circ$ .

As the reaction proceeds, the active alcoholate is partly converted into alcoholate of the inactive alcohol and free active alcohol, with a resulting change in the rotation. The course of the reaction can be followed



by determining graphically the percentage of free active alcohol and active alcoholate. Fig. 1 gives the curve for the rotation of mixtures of *l*-amyl alcohol and chloral-*l*-amylalcoholate; Fig. 2, that for *d*-sec.butyl alcohol and butylchloral-*d*-sec.butylalcoholate. The ordinates represent the angles of rotation and the abscissae, from left to right, the percentages of active alcohol. The curves are not linear as assumed by Kuntze.

It is to be observed that these curves were determined for solutions containing only the optically active substances, whereas in the following

experiments, where the curves were used for determining the end points of reactions, other (optically inactive) substances were present which might affect the rotations. It will be seen, however, that the absolute value of the equilibrium point of the reactions is not the matter of primary importance, but rather the order in which the end points with the different alcohols fall. The end point of the reaction cannot, in fact, be exactly determined by the method used since, on account of the high velocity of the interaction between the alcohols and alcoholates concerned, it is impossible to determine the correction to be applied to the observed rotation for the effect of all the substances in the solutions on the rotatory power of the optically active substances. It can be shown, however, that there is no reason to suspect any disturbance from this cause which

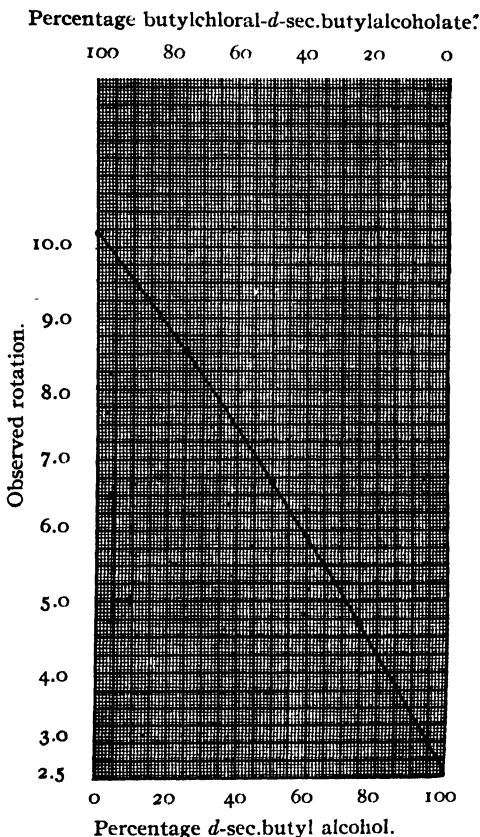


Fig. 2.

could affect the order in which the end points with the various alcohols fall. In the case of alcohols sufficiently near together in the series, so that such slight disturbances would be of consequence, the nature and concentration of the substances present is either the same, or so nearly so, that this effect upon the rotation of the active compounds present should be the same. The following tests confirm this expectation. It will be seen that the rotatory power of *d*-sec.butyl alcohol is unaffected by the

presence of other alcohols. In the case of butylchloral-*d*-sec.butylalcoholate the rotation is affected by other alcoholates, but the effect is small and is the same for the alcoholates tried.

The following experiments were carried out in 20 cc. of benzene solution at concentrations approximately the same as those occurring in the experiments below:

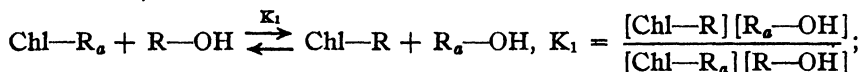
	$\alpha_D^{25^\circ}$
0.5 $\times$ 0.025 mol <i>d</i> -sec.butyl alcohol.....	1.28°
Upon addition of 0.5 $\times$ 0.025 mol methylisobutylcarbinol.....	1.28°
Upon addition of 0.5 $\times$ 0.025 mol methylisopropylcarbinol.....	1.28°
0.68 $\times$ 0.025 mol <i>d</i> -sec.butyl alcohol.....	1.77°
Upon addition of 0.32 $\times$ 0.025 mol ethyl alcohol.....	1.77°
Upon addition of 0.32 $\times$ 0.025 mol <i>n</i> -propyl alcohol.....	1.77°

The following experiments were carried out with a specimen of butylchloral-*d*-sec.butylalcoholate differing slightly in rotatory power from the purest product, but the similarity in effect in the two cases is unmistakable.

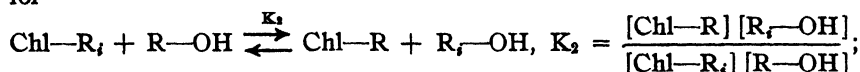
0.5 $\times$ 0.025 mol. active alcoholate.....	4.78°
Upon addition of 0.5 $\times$ 0.025 mol alcoholate of methylisobutylcarbinol.....	4.84°
Upon addition of 0.5 $\times$ 0.025 mol alcoholate of methylisopropylcarbinol.....	4.84°

It appears certain that, although the end point of the reaction cannot be exactly determined, the order in which the end points with the different alcohols fall must be correctly given.

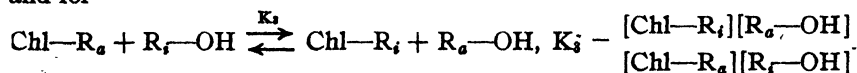
Marckwald<sup>1</sup> probably obtained *l*-amyl alcohol pure, finding  $[\alpha_D^{20^\circ}] = -5.90^\circ$ . For the alcohol used here  $[\alpha_D^{20^\circ}] = -5.496^\circ$  and  $[\alpha_D^{25^\circ}] = -5.428^\circ$ , in benzene solution,  $[\alpha_D^{25^\circ}] = -5.12^\circ$ . The impurity in the *l*-amyl alcohol, a fusel oil product, is not the *d*-isomer, but chiefly isoamyl alcohol, which must be present to the extent of about 6.85%. Since isoamyl alcohol is present, it must enter into all the equilibria, but the following considerations show that its presence cannot change the order of the end points reached with the various aliphatic alcohols. Letting Chl stand for  $\text{CCl}_3\text{CH}(\text{OH})\text{O}-$ ,  $\text{R}_a$  for the active amyl radical,  $\text{R}_i$  for the isoamyl radical,  $\text{R}$  for any inactive radical; and indicating the equilibrium constants by  $\text{K}_1$ ,  $\text{K}_2$ , and  $\text{K}_3$ , and the concentrations by expressions in brackets; for the reaction,



for



and for



Hence

$$\frac{K_1}{K_2} = \frac{[\text{Chl}-R_i][R_a-\text{OH}]}{[\text{Chl}-R_a][R_i-\text{OH}]} = K_3, \text{ and } \frac{[\text{Chl}-R_i]}{[\text{Chl}-R_a]} = K_3 \frac{[R_i-\text{OH}]}{[R_a-\text{OH}]}$$

The ratio of the isoamyl- and active amylalcoholates must, therefore, remain proportional to the ratio of the isoamyl and active amyl alcohols, independently of the nature of the alkyl radical R.

TABLE II.  
Primary alcohols.  
Butylchloral-*d*-sec.butylalcoholate.

Formula.	$\overset{\text{H}}{\underset{ }{\text{H}}}$	$\overset{\text{H}}{\underset{ }{\text{H}}}$	$\overset{\text{H}}{\underset{ }{\text{H}}}$	$\overset{\text{H}}{\underset{ }{\text{H}}}$	$\overset{\text{H}}{\underset{ }{\text{H}}}$	$\overset{\text{H}}{\underset{ }{\text{H}}}$	$\overset{\text{H}}{\underset{ }{\text{H}}}$	$\alpha_D^{25^\circ}$	Pct. act. alcohol.
C <sub>2</sub> H <sub>5</sub> OH.....							3 2	+5.20°	68.8%
C <sub>4</sub> H <sub>9</sub> OH.....				3	2	2	2	5.24	68.4
C <sub>5</sub> H <sub>11</sub> OH.....					3	2	2	5.28	67.8
C <sub>7</sub> H <sub>15</sub> OH.....	3	2	2	2	2	2	2	5.29	67.7
C <sub>8</sub> H <sub>17</sub> OH.....		3	2	2	2	2	2	5.30	67.6
(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> OH.....					6	1	2	5.33	67.3

Chloral-*d*-amylalcoholate.

C <sub>7</sub> H <sub>15</sub> OH.....	3	2	2	2	2	2	2	-0.025°	51.2%
C <sub>8</sub> H <sub>17</sub> OH.....		3	2	2	2	2	2	-0.020	50.9
C <sub>2</sub> H <sub>5</sub> OH.....						3	2	+0.065	45.9
C <sub>3</sub> H <sub>7</sub> OH.....					3	2	2	0.075	45.3
(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> OH.....					6	1	2	0.085	44.7
C <sub>4</sub> H <sub>9</sub> OH.....				3	2	2	2	0.095	44.1
CH <sub>3</sub> OH.....							3	0.120	42.6
(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CH <sub>2</sub> OH.....					6	1	2	0.190	38.1

Secondary alcohols.  
Butylchloral-*d*-sec.butylalcoholate.

	$\overset{5}{\underset{ }{\text{H}}}$	$\overset{4}{\underset{ }{\text{H}}}$	$\overset{3}{\underset{ }{\text{H}}}$	$\overset{2}{\underset{ }{\text{H}}}$		
(CH <sub>3</sub> ) <sub>2</sub> CHOH.....				6	1	6.23°
CH <sub>3</sub> \ CHOH.....				3	5	6.42
C <sub>2</sub> H <sub>5</sub> \ CHOH.....						53.6
CH <sub>3</sub> \ CHOH.....				3	2	6.44
n-C <sub>2</sub> H <sub>7</sub> \ CHOH.....					5	53.2
CH <sub>3</sub> \ CHOH.....				6	1	6.46
(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> \ CHOH.....					5	52.9
CH <sub>3</sub> \ CHOH.....				6	4	6.50
(CH <sub>3</sub> ) <sub>2</sub> CH \ CHOH.....					1	52.4
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> CHOH.....				6	4	6.52
CH <sub>3</sub> \ CHOH.....					1	52.0
(CH <sub>3</sub> ) <sub>3</sub> C \ CHOH.....				9	3	6.74
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> CHOH.....						49.6
[(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> ] <sub>2</sub> CHOH.....				6	4	6.86
				12	2	7.27
					4	42.5

Chloral-*l*-amylalcoholate.

	5 H	4 H	3 H	2 H.	$\alpha_D^{25^\circ}$	Pct. act. alcohol.
$(CH_3)_2CHOH$ .....			6	1	0.290°	31.7%
$CH_3 \begin{array}{l} \diagup \\ \diagdown \end{array} CHO$ .....						
$C_2H_5 \begin{array}{l} \diagup \\ \diagdown \end{array} CHO$ .....		3	5	1	0.300	30.9
$(C_2H_5)_2CHOH$ .....		6	4	1	0.365	26.5
$CH_3 \begin{array}{l} \diagup \\ \diagdown \end{array} CHO$ .....						
$(CH_3)_2CH \begin{array}{l} \diagup \\ \diagdown \end{array} CHO$ .....		6	4	1	0.370	26.0
$CH_3 \begin{array}{l} \diagup \\ \diagdown \end{array} CHO$ .....						
$(CH_3)_3C \begin{array}{l} \diagup \\ \diagdown \end{array} CHO$ .....		9	3	1	0.380	25.2
$CH_3 \begin{array}{l} \diagup \\ \diagdown \end{array} CHO$ .....						
$n-C_3H_7 \begin{array}{l} \diagup \\ \diagdown \end{array} CHO$ .....	3	2	5	1	0.400	23.9
$CH_3 \begin{array}{l} \diagup \\ \diagdown \end{array} CHO$ .....						
$(CH_3)_2CHCH_2 \begin{array}{l} \diagup \\ \diagdown \end{array} CHO$ .....	6	1	5	1	0.410	23.1
$(C_3H_7)_2CHOH$ .....	6	4	4	1	0.420	22.5
$[(CH_3)_2CHCH_2]_2CHOH$ .....	12	2	4	1	0.450	20.3

## Tertiary alcohols.

Butylchloral-*d*-sec.butylalcoholate.

	5 H	4 H	3 H	2 H.		
$(CH_3)_3COH$ .....			9	0	8.41°	26.8%
$(CH_3)_2 \begin{array}{l} \diagup \\ \diagdown \end{array} COH$ .....						
$C_2H_5 \begin{array}{l} \diagup \\ \diagdown \end{array} COH$ .....		3	8	0	8.53	25.2
$(CH_3)_2 \begin{array}{l} \diagup \\ \diagdown \end{array} COH$ .....						
$n-C_3H_7 \begin{array}{l} \diagup \\ \diagdown \end{array} COH$ .....	3	2	8	0	8.68	23.1
$(CH_3)_2 \begin{array}{l} \diagup \\ \diagdown \end{array} COH$ .....						
$(CH_3)_2CHCH_2 \begin{array}{l} \diagup \\ \diagdown \end{array} COH$ .....	6	1	8	0	8.75	22.0
$CH_3 \begin{array}{l} \diagup \\ \diagdown \end{array} COH$ .....						
$(C_2H_5)_2 \begin{array}{l} \diagup \\ \diagdown \end{array} COH$ .....		6	7	0	8.86	20.6

Chloral-*l*-amylalcoholate.

	5 H	4 H	3 H	2 H.		
$(CH_3)_3COH$ .....			9	0	0.620°	7.7%
$(CH_3)_2 \begin{array}{l} \diagup \\ \diagdown \end{array} COH$ .....						
$C_2H_5 \begin{array}{l} \diagup \\ \diagdown \end{array} COH$ .....		3	8	0	0.630	6.9
$CH_3 \begin{array}{l} \diagup \\ \diagdown \end{array} COH$ .....						
$(C_2H_5)_2 \begin{array}{l} \diagup \\ \diagdown \end{array} COH$ .....		6	7	0	0.635	6.6
$(CH_3)_2 \begin{array}{l} \diagup \\ \diagdown \end{array} COH$ .....						
$n-C_3H_7 \begin{array}{l} \diagup \\ \diagdown \end{array} COH$ .....	3	2	8	0	0.640	6.0
$(CH_3)_2 \begin{array}{l} \diagup \\ \diagdown \end{array} COH$ .....						
$CH_3 \begin{array}{l} \diagup \\ \diagdown \end{array} COH$ .....						
$(CH_3)_2CHCH_2 \begin{array}{l} \diagup \\ \diagdown \end{array} COH$ .....	6	1	8	0	0.655	5.9

*d*-Sec.butyl alcohol was also probably obtained pure by Pickard and Kenyon,<sup>1</sup> who found that  $[\alpha_D^{27}] = +13.52^\circ$  and  $[\alpha_D^{21}] = +13.85^\circ$ ; by interpolation  $[\alpha_D^{25}] = +13.63^\circ$ . For the alcohol used here  $[\alpha_D^{25}] = +13.11^\circ$ , in benzene solution,  $[\alpha_D^{25}] = +14.04^\circ$ . The impurity in the *d*-sec.butyl alcohol is probably chiefly the *l*-isomer which cannot change the order of the end points reached with the different aliphatic alcohols. If the impurity is wholly the *l*-isomer, the *d*-sec.butyl alcohol is 98.08% pure.

Table II gives a list of the aliphatic alcohols which were allowed to react with butylchloral-*d*-sec.butylalcoholate and chloral-*l*-amylalcoholate. The alcohols are arranged in order corresponding to the percentage of active alcohol set free, which is equivalent to the percentage of alcoholate of the inactive alcohols formed. In both series the first column gives the formula of the alcohol; the second column, the number of hydrogen atoms occurring in the various positions in the molecule (explained more fully below); the third column, the average observed rotations; and the fourth column, the percentage of active alcohol set free, determined graphically from Figs. 1 and 2.

### III. Discussion of Results.

It will be seen at once from the foregoing table that the three classes of alcohols fall in separate groups, as in the work of Menshutkin. Also, the change in the end point of the reaction is roughly parallel to the molecular weights of the alcohols. Since, however, there are marked exceptions to the latter statement and since isomeric compounds do not give the same values, it is necessary to look for a more exact basis for the observed relationships.

Passing down the list of alcohols in both series of experiments,  
 $\text{CCl}_3\cdot\text{CH}(\text{OH})\text{O}-\text{C}_5\text{H}_{11} + \text{R}-\text{OH} \rightleftharpoons \text{CCl}_3\cdot\text{CH}(\text{OH})\text{O}-\text{R} + \text{C}_5\text{H}_{11}-\text{OH},$   
 and

$\text{CH}_3\cdot\text{CHCl}\cdot\text{CCl}_2\cdot\text{CH}(\text{OH})\text{O}-\text{C}_4\text{H}_9 + \text{R}-\text{OH} \rightleftharpoons$   
 $\text{CH}_3\cdot\text{CHCl}\cdot\text{CCl}_2\cdot\text{CH}(\text{OH})\text{O}-\text{R} + \text{C}_4\text{H}_9-\text{OH}$

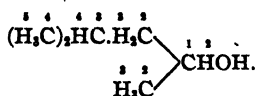
the equilibrium point is gradually shifted to the left. This must mean that the affinity of the alkyl radicals, R, for the hydroxyl group is increasing more than their affinity for the chloral group. The assumption that the affinity for negative groups is increasing in this direction is justified by the investigation carried out in this laboratory and elsewhere on the equilibrium,  $(\text{CH}_3)_2\text{CH}\cdot\text{CHBr} \rightleftharpoons (\text{CH}_3)_3\text{CBr}$ . In the gaseous condition, 18% of isobutyl bromide is in equilibrium with 82% of tertiarybutyl bromide, indicating that the radical in the latter has the greater affinity for bromine. It, therefore, appears reasonable to assume that its affinity will be correspondingly greater for any negative radical;

<sup>1</sup> *J. Chem. Soc.*, 99, 64 (1911).

i. e., that the affinity of the radicals for negative groups increases as we pass downward in the table; the increase with respect to the hydroxyl group, however, is the greater. For the sake of brevity the radicals will be called more positive as we pass downward in the table.

Since in the reactions studied different alkyl radicals are joined to oxygen both in the alcoholates and in the alcohols, the simplest assumption, in view of the affinity of hydrogen for oxygen, would be that the difference in affinity is controlled by the difference in the number and position of the hydrogen atoms in the molecule. A consideration of the results will be seen to justify this point of view.

The position of the hydrogen atoms will be designated by their relation to the carbon atom united with the hydroxyl or chloral group. Some scale must be adopted which expresses the relative influence of hydrogen atoms in different positions upon the affinity of the radical. According to van't Hoff<sup>1</sup> the total influence which two atoms in a molecule have on each other can be separated into two effects, the indirect action exerted along the carbon chain and the direct action exerted through space. Michael,<sup>2</sup> not discriminating between these two effects, uses a scale which represents the sum of the direct and indirect influences of all the atoms of a normal organic compound upon any given atom. The following scale represents the order of decreasing influence: 1-2-3-5-6-4-7-(9-10-11)-8. The carbon atom joined to the —OH radical is taken as 1 and the other atoms are numbered according to their degree of removal from carbon atom 1; thus, for example, in methylisobutylcarbinol,



It is to be noticed that according to this scale the atoms in Position 4 have relatively less effect than those in Positions 5 and 6. This assumption, among others, is tested by the results obtained in this investigation.

The alcohols were all purified with care and an examination of the results seems to indicate that none of the differences in the amounts of active alcohol displaced can be the result of impurities.<sup>3</sup> As will be seen, all the important conclusions are based on comparatively large differences.

(a) Within the first five positions the replacement of hydrogen by methyl, which introduces three hydrogen atoms into the position next further removed, always increases the positive character of the radical, so that less active alcohol is displaced. Since, however, the *primary, secondary,*

<sup>1</sup> *Ansichten über organische Chemie*, 1, 284; 2, 252 (1878).

<sup>2</sup> *J. prakt. Chem.*, N. S., 60, 331 (1899); *Ber.*, 39, 2139 (1906).

<sup>3</sup> The smallest difference could be accounted for only by over 1% of impurity, which is entirely improbable, although further work on some of the alcohols is now in progress.

and tertiary alcohols fall in three separate groups, it appears that the replacement of a hydrogen atom in Position 2, H, by a methyl group in Position 2-3, CH<sub>3</sub>, is much more effective in increasing the positive character of the alkyl radicals than any alteration in their structure and composition which leads to the replacement of H by CH<sub>3</sub>, or of H by CH<sub>3</sub>.

(b) Three hydrogen atoms in Position 4 are more effective than one in Position 3, although Position 4 is relatively weak according to the scale adopted.

Whenever H is replaced by CH<sub>3</sub> there is an increase in the positive character of the radical, less active alcohol being displaced. Examples of this are, ethyl and *n*-propyl alcohols; isopropyl and *s*-butyl alcohols; methylisopropyl- and methyl-*t*-butylcarbinols; and *t*-butyl and *t*-amyl alcohols. The differences between the end points are considerably greater in the butylchloral than in the chloral series, which is a result of the relatively greater importance of Position 4 in the former.

(c) The relatively small influence of atoms in Position 4 as compared with those in Position 5, as predicted by Michael, can be clearly seen in the chloral series. In the first place, the replacement of H by CH<sub>3</sub> is much more effective than the replacement of H by CH<sub>3</sub>. For example, the change in passing from *n*-propyl to *n*-butyl alcohol is greater than that in passing from *n*-propyl to isobutyl alcohol; from *s*-butyl alcohol to methyl-*n*-propylcarbinol greater than from *s*-butyl alcohol to diethylcarbinol; and from *t*-amyl alcohol to dimethyl-*n*-propylcarbinol greater than from *t*-amyl alcohol to diethylmethylcarbinol. Still more striking evidence of the influence of Position 5 is the fact that methyl-*n*-propyl- lies below methyl-*t*-butylcarbinol, as well as the fact that methyl-*n*-propyl- and methylisobutylcarbinols lie below methylisopropyl- and methyl-*t*-butylcarbinols, respectively. It is apparent that the position of the hydrogen atoms has a marked influence upon the positive character of these radicals and that it even outweighs the effect of difference in number of hydrogen atoms in the case of methyl-*n*-propyl- and methyl-*t*-butylcarbinols.

(d) Turning to the butylchloral series, the relative effects of atoms in Positions 4 and 5 appear in most cases to be reversed, which accounts for the most important differences in the two series. In the butylchloral series, *n*-butyl alcohol lies above *n*-propyl and isobutyl alcohols; methyl-*n*-propyl- and methylisobutylcarbinols lie above diethyl- and methylisopropylcarbinols; and dimethyl-*n*-propyl- and dimethylisobutylcarbinols lie above diethylmethylcarbinol. Evidently the spatial arrangement comes into play in some way not accounted for in the scale of influence given above. More definite conclusions can only be reached after other series of equilibria have been investigated.

(e) Looking again at Michael's scale of influence, 1-2-3-5-6-4-7-9-10-11-8-, it will be seen that atoms in Position 8 have much less influence than those in Position 7, so that  $3\text{H}$  may be less influential than H. This would account for the fact that *n*-heptyl alcohol lies above *n*-hexyl alcohol in both series. It is also evident that both Positions 7 and 8 are less effective than Positions 4 and 5 and this may partly explain why *n*-heptyl and *n*-hexyl alcohols lie higher up in both series than would be expected from their comparatively large molecular weights.

(f) Isomeric compounds have quite different end points except when they have the same number of hydrogen atoms in the same positions. The fact that isomeric compounds usually displace different amounts of active alcohol is explained by the fact that their hydrogen atoms are differently situated, as in several of the cases cited under (c) and (d). The resulting differences in the positive character of the radicals is slight, however, in the case of diethyl- and methylisopropylcarbinols, which have the same number of hydrogen atoms in the same positions. In both series the difference between the end points reached with these two alcohols is clearly less than the difference between the end point of either and that of their common isomer, methylisopropylcarbinol, whose hydrogen atoms occupy different positions. It will be noticed, however, that in the chloral series diethylcarbinol lies above methylisopropylcarbinol, whereas the order is reversed in the butylchloral series. Here, again, is evidence of spatial influences not accounted for in the scale adopted.

(g) Whether or not some specific influence of the carbon atoms comes into play can hardly be determined from the results obtained with the alcohols used in this investigation. If, however, carbon has a negative influence, it is doubtless weak as compared with the positive influence of hydrogen. Rather strong evidence of this is furnished by the fact that the replacement of H by  $\text{CH}_3$  increases the positive character of the radical even in the chloral series where Position 4 is weaker than Positions 3 and 5. If the positive character of the radical is still increased, in spite of the fact that the positive H has been replaced by negative C and three hydrogen atoms introduced into the relatively weak Position 4 it is evident that any negative influence due to the carbon must be slight as compared with the positive influence of hydrogen. Michael has considered the effect of the carbon somewhat in detail, but the results given here do not justify any further discussion.

The results may thus be to a considerable extent coördinated on the basis adopted—that the affinity of the aliphatic radicals for negative groups is governed chiefly by the number and position of the hydrogen atoms. It is possible to construct a scale which represents the relative



influence of all the atoms in the molecule, although the scale cannot be exactly the same for the two series.

As stated above, it is concluded that the affinity of the alkyl radicals for hydroxyl increases more than does that for the chloral radical as we pass downward in the table. Obviously, however, since the order of the alcohols is not the same in the two series, neither of them can be assumed to represent the relative affinity of the alkyl radicals for hydroxyl. Nevertheless it is possible that this is represented approximately by the order in either of the series. The order in which these radicals would fall as regards their affinity for the chloral and butylchloral radicals, respectively, is evidently not the same.

If we consider that this increase in the affinity of the alkyl radicals for "negative" radicals is due to increasing "positive" character of the former, it is evident that the degree of this "positive" character is not an absolute property or characteristic of any given radical, but depends upon the structure of the group to which it is joined. This is quite in keeping with the assumption that the affinity for the negative radical is controlled to a considerable extent by attractive forces between the hydrogen atoms and the oxygen or other atoms of the negative group. The position of these hydrogen atoms relative to the carbon by which the alkyl group is united to other groups—the factor chiefly considered above—may thus be in some cases of less significance than their position relative to various other atoms of the molecule. The spatial relationships involved here, as well as the other questions raised above, obviously require much further investigation. The problem, however, appears to be more fundamental and is probably simpler than that of the relation between constitution and reaction velocity.

#### IV. Molecular-weight Determinations with Chloralethylalcoholate.

Since chloralethylalcoholate was found by Beckmann<sup>1</sup> to be dissociated in benzene solutions, it was considered desirable to carry out further molecular-weight determinations at various concentrations in benzene, in order to gain information regarding the condition of the alcoholate at the concentrations at which the foregoing experiments were carried out. At the same time it appeared to be a good opportunity to investigate the behavior of such a nonelectrolytic dissociation in a variety of solvents. Brunner's<sup>2</sup> statement that no dissociation was to be found in any solvent was open to doubt in view of the dissociation known to occur in benzene.

The customary Beckmann apparatus was used, except that the stirrer was provided with a mercury seal to prevent the entrance of moisture and the evaporation of solvent. Without this it was found impossible to obtain accurate results, especially when the solutions were left standing

<sup>1</sup> *Z. physik. Chem.*, **2**, 724 (1888).

<sup>2</sup> *Z. physik. Chem. R.*, **45**, 380 (1903).

for several hours or often for a day or more. The freezing point and dielectric constants were taken from Landolt, Börnstein, and Roth Tabellen (1912).

The molecular weight of chloral itself was first determined in benzene. In a 2.5% solution by weight, the molecular weight of chloral was found to be 164 (calculate 147.4); therefore, chloral is somewhat associated in benzene solution. Since the freezing point did not alter on standing for two days, it is evident that chloral does not react with benzene in any way.

TABLE III.

Chloroethylalcoholate in benzene. Calculated molecular weight 193.4. Freezing point constant 4.9. Dielectric constant 2.288<sup>18°</sup>.

G. solute per 100 g. solvent.	$\Delta$ .	Molecular weight.	Percentage dissociation.	$K \times 10^{-4}$ .
0.15	0.044°	167	15.74%	1.99
0.37	0.109	173	11.99	2.75
0.49	0.142	174	11.15	2.79
0.59	0.166	176	9.61	2.74
0.73	0.206	178	8.41	2.56
1.07	0.295	182	6.38	2.11
1.22	0.331	186	4.21	1.13
2.04	0.543	189	2.30	0.50
5.01	1.276	197	...	...
7.90	1.974	199	...	...
9.23	2.218	208	...	...
13.46	3.026	222	...	...

It was found that the dissociation does not occur instantaneously since, in the more dilute solutions where dissociation was greatest, equilibrium was reached only after several hours, the change in the molecular weight amounting to 10% in some cases. In the solutions where association occurred equilibrium was usually reached immediately; although the value here was sometimes high at first, indicating, as would be expected, that part of the molecules were undergoing dissociation.

For solutions of concentrations 0.37, 0.44 and 0.59%, the dissociation is evidently taking place in accordance with the law of mass action. The values of the dissociation constant  $K = \frac{[CCl_3 \cdot CHO][C_2H_5OH]}{[CCl_3 \cdot CH(OH)O-C_2H_5]}$ , are in fairly good agreement, 2.74, 2.79 and  $2.74 \times 10^{-4}$ . For more concentrated solutions the value of the dissociation constant gradually decreases, which is readily accounted for by the fact that association has already begun to take place to an appreciable degree. In solutions of the concentration 5.01% association predominates. The concentrations of alcoholate in the equilibrium determinations was always considerably greater than this.

There seems to be, in general, no evidence of any definite relation between association and optical rotation,<sup>1</sup> but, in any case, since the re-

<sup>1</sup> Turner, "Molecular Association," p. 104 (1915).

sulting rotations were referred to an empirical curve any disturbance from this cause would be eliminated.

TABLE IV.

## Chloralethylalcoholate in bromoform.

Freezing-point constant = 14.4.			Dielectric constant = $4.51^{20^\circ}$ .		
G. solute per 100 g. solvent.	$\Delta$ .	Molecular weight.	G. solute per 100 g. solvent.	$\Delta$ .	Molecular weight.
0.42	$0.332^\circ$	182.6	1.54	$1.072^\circ$	208
0.44	$0.351^\circ$	183.1	5.14	$3.016^\circ$	246
1.04	$0.761^\circ$	198	5.55	$3.193^\circ$	250

## Chloralethylalcoholate in nitrobenzene.

Freezing-point constant = 7.05.		Dielectric constant = $36.45^{18^\circ}$ .	
G. solute per 100 g. solvent.	$\Delta$ .	Molecular weight.	
2.05	$0.700^\circ$	205	

## Chloralethylalcoholate in ethylene bromide.

Freezing-point constant = 11.8.		Dielectric constant = $4.86^{18^\circ}$ .	
G. solute per 100 g. solvent.	$\Delta$ .	Molecular weight.	
0.38	$0.231^\circ$	179	

In Fig. 3 the molecular weight of chloralethylalcoholate is plotted against the concentration of the solution. When extended to more concentrated solutions the curve for benzene bends upward.

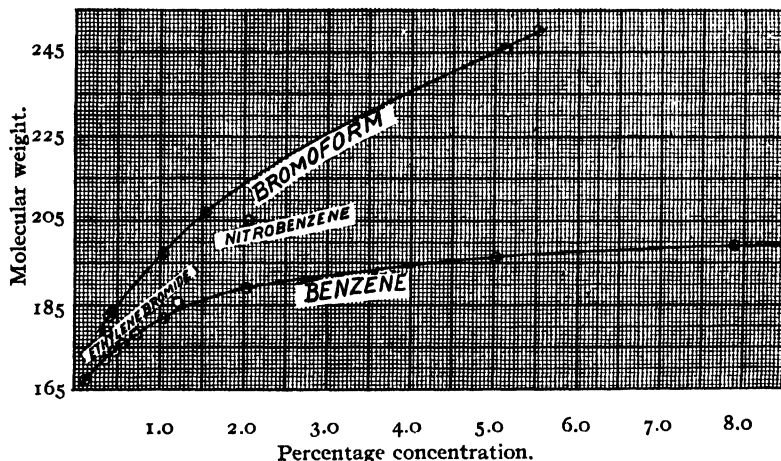


Fig. 3.

It will be seen that the values of the molecular weight in bromoform are higher throughout than in benzene, although the former has a somewhat larger dielectric constant. In a 5.01% benzene solution the molecular weight is 197, whereas in a 5.14% bromoform solution it is 246. The effect of the dielectric constant is more conclusively tested by the determination of the molecular weight in nitrobenzene. It was found that chloralethylalcoholate is no more dissociated in nitrobenzene of high dielectric constant than in the solvents whose dielectric constants are comparatively

low. Table V gives a comparison of the values of the molecular weight of chloraethylalcoholate in the various solvents with their dielectric constants, the values being read from the curve in the case of bromoform.

TABLE V.

Solvent.	D. E.	Conc.	Mol. wt.	Conc.	Mol. wt.
Benzene.....	2.288	2.04	189	0.37	173
Nitrobenzene.....	36.450	2.05	205	....	...
Bromoform.....	4.510	2.05	215	0.38	182
Ethylene bromide.....	4.860	....	...	0.38	179

### V. Experimental.

***l*-Amyl Alcohol.**—*l*-Amyl alcohol was dried by boiling with lime for two days and was carefully fractionated with a column of beads. B. p. 128–128.05° (760 mm.).  $\alpha_D^{25} = -4.43^\circ$ ,  $d_4^{25} = 0.8152$ ,  $[\alpha_D^{25}] = -5.428^\circ$ ;  $\alpha_D^{20} = -4.49^\circ$ ,  $d_4^{20} = 0.8169$ ,  $[\alpha_D^{20}] = -5.496^\circ$ . The rotation of the pure alcohol given by Marckwald<sup>1</sup> is  $[\alpha_D^{20}] = -5.90^\circ$ . The alcohol used here is 93.15% pure, and the impurity is doubtless isoamyl alcohol as discussed above.

***d*-Sec.butyl Alcohol.**—*dl*-Sec.butyl alcohol was prepared by the reduction of methylethyl ketone by hydrogen according to Ipatiew's method. The reduction occurred at 180–200° with nickel oxide as catalyst. *d*-Sec.butyl alcohol was obtained by the method recently described by Pickard and Kenyon<sup>2</sup> and the separation was carried out in most respects according to their description. It was found, however, (a point not noted by them) that the solubility of the brucine *s*-butyl phthalate in acetone was greatly influenced by the amount of water present. It was found necessary to add 30–50 cc. of water to a liter of acetone to bring about solution in the proportion specified by them. The brucine salt was recrystallized from methyl alcohol seven or eight times until a constant rotation was obtained for a sample containing 1 g. salt in 50 cc. absolute ethyl alcohol. The specific rotation of the salt usually obtained was  $[\alpha_D] = -4.62^\circ$ . The value given by Pickard and Kenyon is  $[\alpha_D] = -2.93^\circ$ . Since the *d*-sec.butyl alcohol proved to have a lower rotation than that obtained by Pickard and Kenyon, it is evident that a complete separation was not obtained, although the rotation of the brucine salt did not change on further recrystallization. It appears possible that the brucine used contained other alkaloids which interfered with the separation. The *d*-sec.butyl alcohol was dried with fused potassium carbonate and by boiling with lime for three days, and was then carefully fractionated with a column of beads. B. p. 98.7–99.1° (760 mm.).  $\alpha_D^{25} = +10.53^\circ$ ;  $d_4^{25} = 0.8034$ ;  $[\alpha_D^{25}] = +13.11^\circ$ . The value given by Pickard and Kenyon (obtained by interpolation between the values given for 21°

<sup>1</sup> *Ber.*, 34, 485 (1901).

<sup>2</sup> *J. Chem. Soc.*, 103, 1923 (1913).

and  $27^\circ$ ) is  $[\alpha_D^{25}] = +13.63^\circ$ . The impurity in the alcohol is probably the *l*-isomer.

**Chloral** was obtained by distilling pure chloral twice from sulfuric acid, care being taken to protect it from moisture. B. p.  $97.3\text{--}97.8^\circ$  (760 mm.).

**Butylchloral** was prepared from butylchloral hydrate, which was dehydrated by shaking with sulfuric acid in a separating funnel. The upper layer, consisting of the butylchloral, was removed and treated with powdered lime to remove any sulfuric acid which might be present, and carefully protected from moisture during the subsequent fractionation. B. p.  $164.5\text{--}165.5^\circ$  (760 mm.).

**Chloral-*l*-amylalcoholate** and **butylchloral-*d*-sec.butylalcoholate** are colorless liquids, prepared by mixing equimolecular quantities of the active alcohol and the aldehyde. Since the union is accompanied by a large evolution of heat, the liquids were cooled in ice and salt and protected from moisture as much as possible while they were being mixed.

**Chloralethylalcoholate** was recrystallized twice from benzene and dried in a desiccator. It was introduced into the solvent in the form of pellets. M. p.  $50^\circ$ .

The primary alcohols were all good commercial products, carefully dried by boiling with lime and fractionated with a column of beads.<sup>1</sup>

*Methyl alcohol*. B. p.  $64.7^\circ$ .      *n-Butyl alcohol*. B. p.  $117.55\text{--}117.95^\circ$ .  
*Ethyl alcohol*. B. p.  $78.0^\circ$ .      *n-Hexyl alcohol*. B. p.  $155.2\text{--}155.7^\circ$ .  
*n-Propyl alcohol*. B. p.  $97.1\text{--}97.4^\circ$ .      *n-Heptyl alcohol*. B. p.  $172.5\text{--}173.5^\circ$ .  
*Isobutyl alcohol*. B. p.  $107.85\text{--}107.95^\circ$ .

**Isoamyl alcohol**, from a commercial product containing 15% of active amyl alcohol, was obtained nearly pure by Marckwald's urethane process.<sup>2</sup> The alcohol was converted into its urethane which was recrystallized from ligroin. Isoamyl urethane which, is much the less soluble, was obtained very nearly free from active amyl urethane after one recrystallization. The alcohol so obtained had a specific rotation of  $[\alpha_D] = -0.048^\circ$ , thus containing about 0.81% of active amyl alcohol. B. p.  $131.2\text{--}131.6^\circ$ .

The secondary alcohols, with the exception of diethylcarbinol, were all obtained by the reduction of ketones according to Ipatiew's method. Alcohols prepared in this way always contain some ketone which can be detected by the sodium nitroprusside test. This test is sensitive to one part of acetone in 1000, but is somewhat less sensitive to the other ketones. The alcohols can be freed from ketone in either of the two following ways: by treatment with phenylhydrazine according to Michael's<sup>3</sup> method or by treatment with *p*-nitrophenylhydrazine, which has the great advantage of remaining behind during the subsequent distillation. The alcohols

<sup>1</sup> The boiling points of all the alcohols are corrected to 760 mm.

<sup>2</sup> *Ber.*, 37, 1040 (1904).

<sup>3</sup> *Ibid.*, 42, 3157 (1909).

were all carefully dried by boiling with lime and fractionated with a column of beads.

**Isopropyl alcohol** was prepared by the reduction of acetone. It was treated with *p*-nitrophenylhydrazine and gave no test for ketone. B. p. 82.5–82.7°.

***s*-Butyl alcohol** was prepared by the reduction of methylethyl ketone and treated with phenylhydrazine. It gave no test for ketone. B. p. 98.4–99.0°.

**Methylisopropylcarbinol** was prepared by the reduction of methylisopropyl ketone. The alcohol was fractionated repeatedly and gave only a slight test for ketone. B. p. 112.9–113.9°.

**Methylpropylcarbinol** was prepared by the reduction of methylpropyl ketone, obtained from acetic ester. The alcohol was given the phenylhydrazine treatment. B. p. 118.9°.

**Methylisobutylcarbinol** was prepared by the reduction of mesityl oxide, which was obtained by boiling diacetone alcohol with a trace of iodine as described by Hibbert.<sup>1</sup> The alcohol was treated with phenylhydrazine. B. p. 130–131°.

**Methyl-*t*-butylcarbinol** was prepared by the reduction of pinacoline. The alcohol was purified by freezing out twice and gave no test for ketone. B. p. 120–120.6°.

**Di-*n*-propylcarbinol** was prepared by the reduction of di-*n*-propyl ketone. The di-*n*-propyl ketone was obtained from *n*-butyric acid by the method of Senderens<sup>2</sup> by passage over thorium oxide at 400–420°. The alcohol was well fractionated and gave no test for ketone. B. p. 154–155°.

**Diisobutylcarbinol** was prepared by the reduction of diisobutyl ketone. The latter was obtained from isovaleric acid catalytically as above. The alcohol was treated with *p*-nitrophenylhydrazine. B. p. 171.4–173.4°.

**Diethylcarbinol** was prepared by the Grignard reaction from ethyl formate and ethyl bromide. B. p. 114.8–115.2°.

***t*-Butyl alcohol.** Kahlbaum's *t*-butyl alcohol was purified by freezing out twice, and then dried and fractionated.<sup>3</sup> B. p. 81.7–82.1°.

***t*-Amyl alcohol** was prepared from amylene by Wyschnegradsky's<sup>4</sup> method. B. p. 101.7–102.1°.

**Diethylmethylcarbinol** was prepared by the Grignard reaction from ethyl bromide and ethyl acetate. B. p. 122.1–122.9°.

**Dimethylpropylcarbinol** was prepared by the Grignard reaction from methyl iodide and ethyl butyrate. B. p. 122.1–122.6°.

**Dimethylisobutylcarbinol** was prepared by the Grignard reaction from acetone and isobutyl iodide. B. p. 132–133°.

<sup>1</sup> THIS JOURNAL, 37, 1748 (1915).

<sup>2</sup> Ann. chim. phys., [8] 28, 243 (1913).

<sup>3</sup> This alcohol was probably not thoroughly dried.

<sup>4</sup> Ann., 190, 332 (1878).

OBSERVED ROTATIONS OF THE MIXTURES OF CHLORAL-*L*-AMYLALCOHOLATE AND *L*-AMYL ALCOHOL FROM WHICH THE CURVE IN FIG. 1 WAS CONSTRUCTED.

Molar pct. alcoholate.	Molar pct. alcohol.	Observed rotations.	
		—1.130°	—1.130°
0%	100%		
20	80	0.645	...
30	70	0.420	0.420
40	60	0.200	...
50	50	0.000	0.000
60	40	+0.160	...
80	20	0.455	+0.455
100	0	0.720	0.720

OBSERVED ROTATIONS OF THE MIXTURES OF BUTYLCHLORAL-*d*-SEC.BUTYLALCOHOLATE AND *d*-SEC.BUTYL ALCOHOL FROM WHICH THE CURVE GIVEN IN FIG. 2 WAS CONSTRUCTED.

Molar pct. alcoholate.	Molar pct. alcohol.	Observed rotations.	
		+2.600°	+2.600°
0%	100%		
25	75	4.700	4.700
50	50	6.700	...
75	25	8.550	8.550
100	0	10.200	10.200

DETERMINATIONS MADE WITH CHLORAL-*L*-AMYLALCOHOLATE.

Inactive alcohol.	$\alpha$ .		Average.	Pct. act. alcohol.
<i>n</i> -Heptyl alcohol.....	—0.025°	...	—0.025°	51.2%
<i>n</i> -Hexyl alcohol.....	0.020	...	0.020	50.9
Ethyl alcohol.....	+0.060	+0.070°	+0.065	45.9
<i>n</i> -Propyl alcohol.....	0.075	0.075	0.075	45.3
Isobutyl alcohol.....	0.085	0.085	0.085	44.7
<i>n</i> -Butyl alcohol.....	0.090	0.100	0.095	44.1
Methyl alcohol.....	0.120	0.120	0.120	42.6
Isoamyl alcohol.....	0.190	0.190	0.190	38.1
Isopropyl alcohol.....	0.290	0.290	0.290	31.7
<i>s</i> -Butyl alcohol.....	0.300	0.300	0.300	30.9
Diethylcarbinol.....	0.365	0.365	0.365	26.5
Methylisopropylcarbinol.....	0.370	0.370	0.370	26.0
Methyl- <i>t</i> -butylcarbinol.....	0.380	0.380	0.380	25.2
Methyl- <i>n</i> -propylcarbinol.....	0.395	0.405	0.400	23.9.
Methylisobutylcarbinol.....	0.410	0.410	0.410	23.1
Di- <i>n</i> -propylcarbinol.....	0.420	0.420	0.420	22.5
Diisobutylcarbinol.....	0.445	0.455	0.450	20.3
<i>t</i> -Butyl alcohol.....	0.620	0.620	0.620	7.7
<i>t</i> -Amyl alcohol.....	0.630	0.630	0.630	6.9
Diethylmethylcarbinol.....	0.635	0.635	0.635	6.6
Dimethyl- <i>n</i> -propylcarbinol.....	0.640	0.640	0.640	6.0
Dimethylisobutylcarbinol.....	0.650	0.660	0.655	4.9

DETERMINATIONS MADE WITH BUTYLCHLORAL-*d*-SEC.BUTYLALCOHOLATE.

Inactive alcohol.	$\alpha$ .		Average.	Pct. act. alcohol.
Ethyl alcohol.....	+5.200°	+5.200°	+5.200°	68.8%
<i>n</i> -Butyl alcohol.....	5.240	5.240	5.240	68.4
<i>n</i> -Propyl alcohol.....	5.280	...	5.280	67.8
<i>n</i> -Heptyl alcohol.....	5.290	...	5.290	67.7
<i>n</i> -Hexyl alcohol.....	5.300	...	5.300	67.6
Isobutyl alcohol.....	5.335	5.325	5.330	67.3
Isopropyl alcohol.....	6.230	6.230	6.230	56.0
<i>s</i> -Butyl alcohol.....	6.420	...	6.420	53.6
Methyl- <i>n</i> -propylcarbinol.....	6.440	6.440	6.440	53.2
Methylisobutylcarbinol.....	6.460	6.460	6.460	52.9
Methylisopropylcarbinol.....	6.495	6.505	6.500	52.4
Diethylcarbinol.....	6.530	...	6.530	52.0
Methyl- <i>t</i> -butylcarbinol.....	6.740	6.740	6.740	49.6
Di- <i>n</i> -propylcarbinol.....	6.860	...	6.860	47.8
Diisobutylcarbinol.....	7.270	...	7.270	42.5
<i>t</i> -Butyl alcohol.....	8.405	8.415	8.410	26.8
<i>t</i> -Amyl alcohol.....	8.530	...	8.530	25.2
Dimethyl- <i>n</i> -propylcarbinol.....	8.680	...	8.680	23.1
Dimethylisobutylcarbinol.....	8.750	...	8.750	22.0
Diethylmethylcarbinol.....	8.860	8.860	8.860	20.6

## Purification of Solvents.

**Benzene** was frozen out six times, dried with calcium chloride and phosphorus pentoxide, and fractionated. B. p. 79.4°.

**Nitrobenzene** was frozen out eight times, dried with calcium chloride, and fractionated. B. p. 210.6–210.8°.

**Bromoform** was frozen out six times, dried with calcium chloride, and fractionated. B. p. 146.6–147.5°.

**Ethylene bromide** was frozen out four times, dried with phosphorus pentoxide, and fractionated. B. p. 131.2–131.4°.

## Summary.

The equilibrium point has here been determined for the reversible reaction of chloral-*l*-amyl alcoholate and butylchloral-*d*-sec.butylalcoholate, respectively, with an extended series of aliphatic alcohols, the optically active alcohol being in each case partially displaced from its combination with the aldehyde by the other alcohol. The equilibrium point of the reaction varies with the alcohol taking part in the reaction, and the order in which the alcohols fall is not the same, although nearly so, in the two series.

The significance of the results as regards the affinities between the radicals concerned is discussed, and an attempt is made to establish a relationship between the constitution of the alcohol radicals and the end point attained in the above reactions.



The degree of dissociation of chloraethylalcoholate into its constituents has been determined in benzene for a wide range of concentrations, and in bromoform, ethylene bromide, and nitrobenzene in fewer concentrations. It is dissociated in dilute solutions, associated in more concentrated ones. There appears to be no relation between the degree of dissociation and the dielectric constant of the solvent.

We take pleasure in acknowledging our indebtedness to the Warren Fund of the American Academy of Arts and Sciences for the excellent polarimeter and spectroscope which were placed at our disposal for this work.

BRYN MAWR, PA.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF KANSAS.]

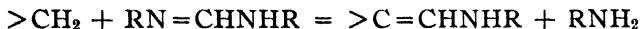
## ON THE REACTIONS OF THE FORMAMIDINES. VI. SOME THIAZOLE DERIVATIVES.

By F. B. DAINS AND A. E. STEPHENSON.

Received June 24, 1916.

Owing to the inability of one of the authors to continue this investigation, it has been deemed best to publish the results already obtained as a preliminary paper in this special field.

It has already been pointed out<sup>1</sup> that compounds containing a methylene grouping react with ease with the substituted formamidines, giving a primary amine and the complex CHNHR in place of the H<sub>2</sub> of the methylene group, as follows:



This occurs not only in the malonic ester, acetoacetic ester and benzyl cyanide type, but also with ring compounds like the pyrazolones and isoxazolones.

In the isothiohydantoin (ketotetrahydro-thiazoles), there is found the complex  $-\text{CO}-\text{CH}_2-\text{S}-$ , which exhibits the general reactions characteristic of an acid methylene grouping, such as aldehyde, phthalic anhydride, nitroso derivatives, etc.

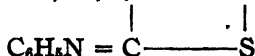
Such compounds should by analogy react with the formamidines; a supposition confirmed by the following experiments:

Diphenyl-isothiohydantoin (2-phenylimido-3-phenyl-4-keto-tetra-hydro-thiazole) was readily obtained by heating in alcohol solution thio-carbanilide and chloroacetic acid. Small amounts of phenyl mustard oil glycolide and phenyl thiourethan were also formed.

Molar quantities of the isothiohydantoin and diphenylformamidine were heated at 140–50° for five hours. The reaction product contained

<sup>1</sup> *Ber.*, 35, 2509 (1902); *THIS JOURNAL*, 31, 1148 (1909); 35, 959, 970 (1913).

aniline, and, in 78% yield, 2-phenylimido-3-phenyl-4-keto-5-anilidomethylene-tetrahydrothiazole,  $C_6H_5N-CO-C=CHNHC_6H_5$



This crystallizes from alcohol in the form of short, pale yellow needles melting at  $202^\circ$ .

Calc. for  $C_{22}H_{17}ON_2$ : N, 11.32%. Found: 11.50%, 11.31%.

**Hydrolysis of the Isothiohydantoin.**—10 g. of the anilidomethylene derivative, 150 cc. alcohol and 15 cc. conc. hydrochloric acid, were heated under a reflux condenser for four hours. The products isolated were (1) diphenyl urea, (2) 2,4-diketo-5-anilidomethylene-tetrahydrothiazole (m. p.  $192^\circ$ ), formed by the hydrolysis of the phenylimido group, obtained also, as will be described later, by the condensation of diphenylformamidine and the diketothiazole, (3) 3-phenyl-2,4-diketotetrahydrothiazole due to further loss of the anilidomethylene group, and (4) aniline hydrochloride.

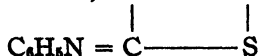
The results thus show a progressive hydrolysis of the molecule. It is of especial interest, however, in this fact that in all the investigations of the anilidomethylene derivatives, this is the first instance noted where that grouping could be split off without complete rupture of the entire molecule.

Di-*o*-tolyl-isothiohydantoin was prepared according to the method of Wheeler and Jamieson.<sup>1</sup> It melts at  $153^\circ$  and gives a benzal derivative melting at  $182.5^\circ$ . It should be noted here that these benzal substitution products can be formed by the direct heating of the aldehyde and hydantoin without the use of any solvent or condensing agent.

Molar quantities of the thiazole and diphenylformamidine, when heated at  $140-50^\circ$  for three hours gave a 75% yield of 2-*o*-tolylimido-3-*o*-tolyl-4-keto-5-anilidomethylenetetrahydrothiazole. From alcohol, this crystallizes in pale yellow, silky needles with a melting point of  $200-1^\circ$ .

Calc. for  $C_{24}H_{19}ON_2S$ : N, 10.53%. Found: 10.44%, 10.65%.

The monosubstituted thiazoles containing a methylene group react in an analogous manner. Thus diphenylformamidine and phenylisothiohydantoin at  $150^\circ$  yielded almost quantitatively 2-phenylimido-4-keto-5-anilidomethylene-tetrahydrothiazole,  $HN-CO-C=CHNHC_6H_5$



It is almost insoluble in alcohol, chloroform, gasoline and benzene, soluble in hot glacial acetic acid, pyridine and nitrobenzene. From the latter solvent it crystallizes in lemon yellow needles melting at  $266.5^\circ$ .

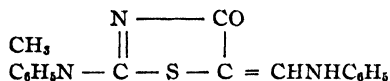
Calc. for  $C_{18}H_{15}ON_2S$ : N, 14.24%. Found: 14.12%, 13.90%.

When phenylisothiohydantoinic acid,  $C_6H_5N=CNH_2-S-CH_2-COOH$ , is heated at  $150-170^\circ$  with diphenyl formamidine, the same

<sup>1</sup> THIS JOURNAL, 25, 369 (1903).

anilidomethylenephénylthiazole (m. p. 266°) is obtained. This involves both ring closure, due doubtless to the high temperature and reaction with the methylene hydrogen. Analogous results were obtained when the same thiohydantoic acid and benzaldehyde were allowed to react at a temperature of 140–50°, though for a few moments the thermometer rose to 200°. The ring was closed and there was formed 2-phenylimido-4-keto-5-benzaltetrahydrothiazole (m. p. 254°), a substance which had been previously obtained by condensing the aldehyde and thiazole in alcohol solution by means of sodium.<sup>1</sup> A similar reaction has been noted<sup>2</sup> in the case of the acetyl or benzoyl thiohydantoic acid, since when this is heated with benzaldehyde, there is formed 1-acyl-2-thio-4-benzalhydantoin.

Another type of thiazole containing a substituted amino group, the 2-methylphenylamido-4-keto-tetrahydrothiazole, was found to condense at 150° with diphenyl formamidine yielding the 2-methyl-phenylamido-4-keto-5-anilidomethylene-tetrahydrothiazole,



This crystallizes from alcohol in reddish granules melting at 180°. It is soluble in hydrochloric acid and reprecipitated by alkalis.

Calc. for  $\text{C}_{17}\text{H}_{16}\text{ON}_2\text{S}$ : N, 13.60%. Found: 13.50%.

**Diketo-thiazoles.**—The presence of two keto groups in the ring seems to have little effect, either in diminishing or increasing the reactivity of the methylene hydrogen. Thus 3-phenyl-2,4-diketo-tetrahydrothiazole was heated with diphenylformamidine at 140–50° for three hours, giving an 80% yield of 3-phenyl-2,4-diketo-5-anilidomethylene-tetrahydrothiazole. This is difficultly soluble in alcohol from which it crystallizes in pale yellow glistening leaflets with a melting point of 192–3°.

Calc. for  $\text{C}_{18}\text{H}_{12}\text{O}_2\text{N}_2\text{S}$ : N, 9.46%. Found: 9.53%, 9.59%.

As has been noted in the early part of this article, this same compound was obtained by the partial hydrolysis of the 2-phenylimido-3-phenyl-anilidomethylene derivative.

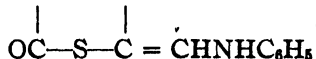
While the above was the main reaction product obtained in heating the thiazole and formamidine, there was also formed a small amount of a compound, soluble in alcohol, melting at 237° and containing 13.11% nitrogen. The data corresponds to that demanded for diphenyl urea, which might readily be formed by the action of aniline on the original thiazole.

**Condensation of an Unsubstituted Diketothiazole.**—Under the same conditions as in previous experiments, a molar mixture of diphenyl formami-

<sup>1</sup> Wheeler and Jamieson, *THIS JOURNAL*, 25, 367 (1903).

<sup>2</sup> Wheeler, Nicolet and Johnson, *Am. Chem. J.*, 46, 469 (1911).

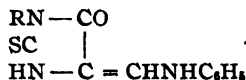
dine and the 2,4-diketo-tetrahydrothiazole gave the 2,4-diketo-5-anilido-methylene-tetrahydrothiazole,  $\text{HN}-\text{CO}$



This is very difficultly soluble in hot alcohol from which it crystallized in almost colorless plates melting at  $233^\circ$ .

Calc. for  $\text{C}_{10}\text{H}_8\text{O}_2\text{N}_2\text{S}$ : N, 12.73%. Found: 12.96%, 13.03%.

As a matter of interest it may be noted here that experiments show that the true thiohydantoin containing a methylene group condense with the formamides giving substituted amino methylene derivatives of the type,



isomeric with the thiazole derivatives.

These investigations are being continued in this laboratory.

LAWRENCE, KANSAS.

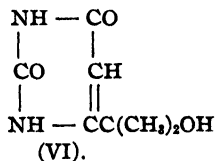
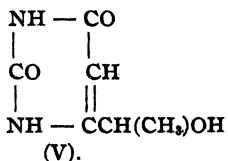
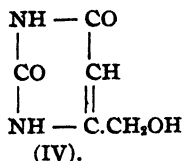
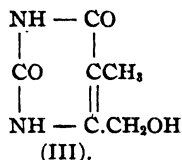
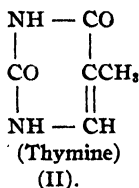
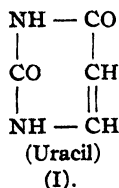
[CONTRIBUTIONS FROM THE SHEFFIELD CHEMICAL LABORATORY OF YALE UNIVERSITY.]

## RESEARCHES ON PYRIMIDINES. LXXXI. SECONDARY-PYRIMIDINE-NUCLEOSIDES AND THEIR UNIQUE BEHAVIOR ON HYDROLYSIS.<sup>1</sup>

BY TREAT B. JOHNSON AND SIDNEY E. HADLEY.

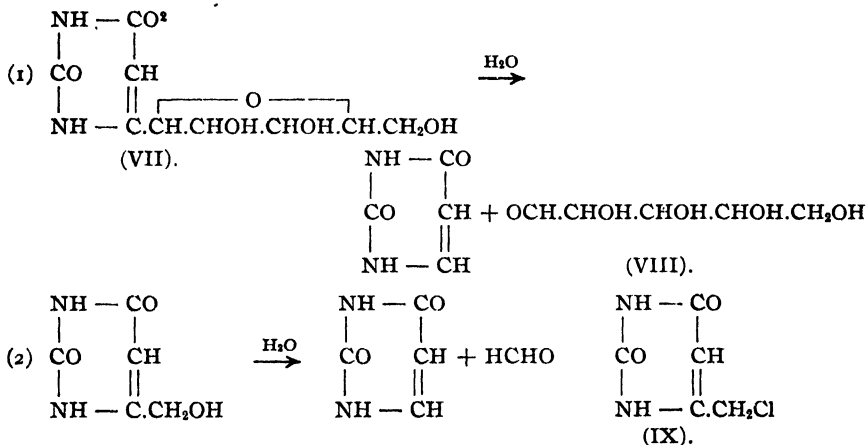
Received June 28, 1916.

This is the fourth paper from this laboratory on pyrimidine nucleosides and, like those preceding it, deals with the chemistry of uracil and thymine combinations containing alcohol groupings in position 4 of the pyrimidine ring. The classification adopted namely, primary, secondary and tertiary



<sup>1</sup> The observations recorded in this paper have developed from an investigation on nucleosides which was originally started in this laboratory by Dr. Lewis H. Chernoff in 1913. The paper has been constructed from a dissertation presented by Mr. Sidney Edward Hadley to the Faculty of the Graduate School of Yale University, 1916, in candidacy for the Degree of Doctor of Philosophy.

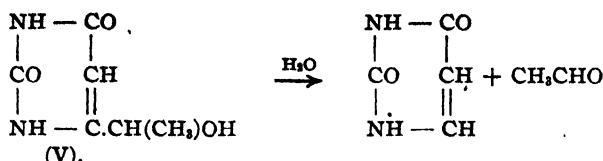
nucleosides, applies to pyrimidine combinations containing the typical alcohol groups represented in Formulas IV, V and VI, respectively. The two primary nucleosides of uracil and thymine (IV and III) have already been synthesized and their chemical behavior investigated.<sup>1</sup> Both compounds are characterized by their stability, and they exhibit the normal behavior of primary alcohols. Neither combination is broken down by heating with acids with rupture of the carbon union in Position 4 of the pyrimidine ring giving uracil and thymine, respectively. Instead of reacting according to Equation 2 the uracil nucleoside (IV) and also the thymine nucleoside (III) interact with acids giving their corresponding alkyl salts, of which the halide (IX) is a typical representative. In other words, pyrimidine alcohols of this type react as might be predicted and do not conform in behavior to that of natural pyrimidine nucleosides like *uridine* (VII). This combination undergoes hydrolysis with acids giving uracil and a sugar.



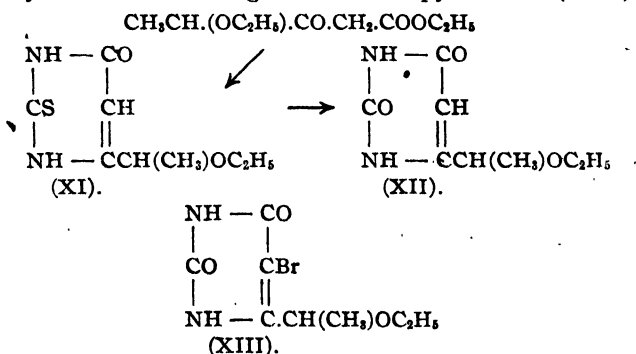
In the light of these interesting results it was of special interest to extend our investigation of these new alcohol combinations and synthesize representatives of secondary nucleosides. Such combinations approach in constitution still closer to that assigned to natural nucleosides (*uridine*), and consequently it was important to determine whether they are less resistant to the action of acids than the primary compounds. The secondary nucleoside (V) was the first representative to be studied, and the primary object of this preliminary paper is to record a characteristic and unique transformation which this combination undergoes on hydrolysis. *It does not interact with acids, under the conditions favorable for the hydrolysis of uridine, with production of uracil and acetaldehyde.*

<sup>1</sup> Johnson and Chernoff, *J. Biol. Chem.*, **14**, 307 (1913); *THIS JOURNAL*, **35**, 585 (1913); **36**, 1742 (1914).

<sup>2</sup> Levene and La Forge, *Ber.*, **45**, 608 (1912).



In order to obtain the nucleoside (V) according to the method already applied successfully in our previous work,<sup>1</sup> it was necessary for us to synthesize first an ether of this nucleoside. The ethyl ether was the derivative selected and was prepared easily in the following manner: Ethyl  $\gamma$ -ethoxy- $\gamma$ -methylacetoacetate<sup>2</sup> (X) was first synthesized in quantity by condensing ethyl  $\alpha$ -ethoxypropionate with ethyl propionate in the presence of metallic sodium (Claisen condensation). This was then allowed to interact with thiourea when they combined smoothly, in the presence of sodium ethylate, giving the 2-thiopyrimidine represented by Formula XI. This pyrimidine was desulfurized by digestion with chloroacetic acid giving the desired nucleoside ether represented by Formula XII. This pyrimidine can be prepared easily in quantity by this method, and proved to be especially suitable for experimental study on account of its purity, crystalline character and insolubility in water. It interacted normally with bromine to give the bromopyrimidine (XIII).

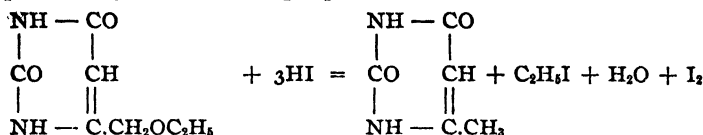


We have now made the most interesting observation that this nucleoside ether (XII) reacts in a characteristic manner when digested with hydrobromic and hydriodic acids. While the ethers of the primary nucleosides, so far examined, interact normally with hydrobromic acid, forming the corresponding alkyl halides and water, this pyrimidine reacts in an entirely different manner, giving a crystalline substance free from halogen and possessing weakly basic properties. Furthermore the pyrimidine (XII) interacts with hydriodic acid giving the same product as is obtained by hydrolysis with hydrobromic acid. This is a very

<sup>1</sup> *Loc. cit.*

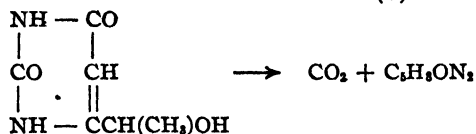
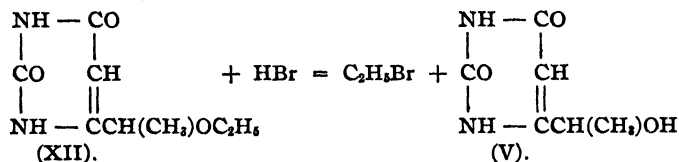
<sup>2</sup> Johnson, *THIS JOURNAL*, 35, 582 (1913); Chernoff, Dissertation, Yale University, 1914.

significant result. The corresponding ethers of primary nucleosides react with this acid with formation of the corresponding alkyl pyrimidines. In other words, such nucleoside combinations are reduced by this reagent as is expressed by the following equation:



The final product of hydrolysis with these halogen acids is not the pyrimidine nucleoside represented by Formula V. Ethyl bromide and ethyl iodide are formed, respectively, during the transformation, as would be expected, but at the same time a secondary reaction sets in during hydrolysis, and a quantity of carbon dioxide is evolved which corresponds to practically one-sixth of the total carbon content of the nucleoside (V). Apparently the nucleoside (V) is the primary product of the reaction, but in this case is unstable in the presence of acids and breaks down further with destruction of the pyrimidine molecule.

This characteristic product of hydrolysis has been isolated, purified and analyzed and we find that it is not identical with uracil. It does not give Wheeler and Johnson's<sup>1</sup> test for this pyrimidine. The analytical values obtained for carbon, hydrogen and nitrogen agree with those required by the empirical formula  $\text{C}_5\text{H}_8\text{ON}_2$ . In other words, we are dealing here with an unique transformation which sharply differentiates secondary from primary nucleosides. The change is accomplished by hydrolysis and may be viewed as a dissociation of the nucleoside into carbon dioxide and the hydrolytic product  $\text{C}_5\text{H}_8\text{ON}_2$  of unknown structure. The complete transformation of the nucleoside ether (XII) is expressed by the following equations:

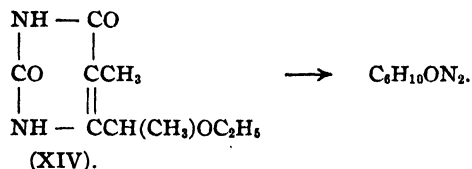


It is an interesting fact that the compound  $\text{C}_5\text{H}_8\text{ON}_2$  and uracil ( $\text{C}_4\text{H}_4\text{O}_2\text{N}_2$ ) both contain the same percentage of nitrogen—25%.

Regarding the structure of this interesting substance  $\text{C}_5\text{H}_8\text{ON}_2$  and the mechanism of its formation from the nucleoside (V), we have not ob-

<sup>1</sup> *J. Biol. Chem.*, **3**, 183 (1907).

tained sufficient data to enable us to formulate definite conclusions. The reaction, however, is apparently a normal one and we already have obtained good evidence that the corresponding nucleoside ether of thymine (XIV) undergoes a similar transformation on hydrolysis, yielding a substance having the formula  $C_6H_{10}ON_2$ . In other words, these two



hydrolytic products are representatives of an homologous series differing in constitution by a  $\text{CH}_2$  radical. A description of our work on secondary thymine nucleoside will be given in a later paper.

A careful search of the literature now reveals the interesting fact that of the 14 known compounds<sup>1</sup> having the formula  $C_5H_8ON_2$  and the 18 conforming to the expression  $C_6H_{10}ON_2$  two agree very closely in chemical and physical properties with our unknown hydrolytic products, namely: 2-oxy-4,5-dimethylimidazol (XV) and 2-oxy-4-ethyl-5-methylimidazol (XVI), respectively.



The imidazol (XV) was first synthesized by Kunne<sup>2</sup> and it is stated by Biltz<sup>3</sup> to darken when heated at  $290^\circ$  and sublime without melting at  $300^\circ$ . Gabriel and Posner<sup>4</sup> assigned to the imidazol (XVI) a decomposition point of  $270^\circ$ . Our hydrolytic product obtained from the nucleoside (V) did not melt at  $300^\circ$  while we find that the corresponding derivative formed by hydrolysis of the pyrimidine (XIV) melts at  $268^\circ$  with decomposition. Owing to lack of time it has been impossible for us to prepare these known imidazols and compare them with our hydrolytic products. This work will be taken up just as soon as possible. Whatever constitution is to be assigned to our hydrolytic products it is apparent that we are dealing here with an unique transformation of the greatest biochemical interest. Our researches on synthetical pyrimidine nucleosides will be continued.

<sup>1</sup> Richter's "Lexikon der Kohlenstoffverbindungen."

<sup>2</sup> *Ber.*, 28, 2040 (1895).

<sup>3</sup> *Ibid.*, 40, 4801 (1907).

<sup>4</sup> *Ibid.*, 27, 1038 (1894).



### Summary.

The secondary nucleoside (V) undergoes hydrolysis, when digested with hydrobromic and hydriodic acids, giving carbon dioxide and a crystalline, basic product  $C_5H_8ON_2$  of unknown constitution.

### Experimental Part.

**Ethyl  $\alpha$ -Ethoxypropionate and Ethyl  $\alpha$ -Methoxypropionate.**—These two esters, which were employed in this investigation, were prepared according to the directions of Schreiner<sup>1</sup> by the action of ethyl  $\alpha$ -bromopropionate on sodium ethylate and sodium methylate, respectively. The  $\alpha$ -bromo ester was prepared from propionic acid according to the directions given by Zelinsky.<sup>2</sup> The reactions in neither case were productive of quantitative yields of the alkoxyl esters. For example, 142 g. and 92 g., respectively, of the purified  $\alpha$ -ethoxy and  $\alpha$ -methoxy esters were obtained from 300 g. of the ethyl  $\alpha$ -bromopropionate.

**Ethyl  $\alpha$ -Methyl- $\gamma$ -methyl- $\gamma$ -ethoxyacetoacetate,  $CH_3CH(OC_2H_5).CO.CH(CH_3)COOC_2H_5$ .** **Preparation of the Ester by Application of Reformatsky's Reaction.**—This  $\beta$ -ketone ester can be prepared by application of Reformatsky's reaction, which has been modified by Johnson<sup>3</sup> and utilized for the preparation of  $\beta$ -ketone esters. Molecular proportions of ethyl  $\alpha$ -ethoxypropionate and ethyl  $\alpha$ -bromopropionate were condensed by warming in the presence of an excess of granulated zinc amalgam. There was an energetic reaction when such a mixture was warmed on a steam bath and, unless retarded, finally became so violent that it was necessary to keep at hand a cooling device to afford proper control of the reaction. After the violent reaction was over, heating on the steam bath was continued for 5–6 hours. To the syrupy liquid thus obtained ice and water were added, when a double zinc combination was precipitated. Keeping the mixture cold with ice, this was decomposed by addition of hydrochloric acid with formation of a clear oil. Ether was then added to dissolve the oil and finally sufficient sodium hydroxide was added to the ether solution to completely dissolve the zinc hydroxide and also the  $\beta$ -ketone ester present. The alkaline solution was saved and on acidifying this with hydrochloric acid, again keeping the solution cold with ice, the free  $\beta$ -ketone ester separated as a red oil. This was extracted with ether, washed with a little water and dried over calcium chloride. We obtained by this procedure 12 g. of the  $\beta$ -ketone ester (undistilled) from 70 g. of ethyl  $\alpha$ -ethoxypropionate, which corresponds to only 12% of a theoretical yield.

**Preparation of the Ester by Application of a Claisen Condensation.**—Molecular proportions of ethyl  $\alpha$ -ethoxypropionate and ethyl propionate

<sup>1</sup> *Ann.*, 197, 13 (1879).

<sup>2</sup> *Ber.*, 20, 2026 (1887).

<sup>3</sup> *THIS JOURNAL*, 35, 582 (1913).

were mixed in a dry flask connected to a return condenser. This was then heated to  $85^{\circ}$  and a molecular proportion of sodium in wire form was added in small portions at a time. Heating was then continued for 3-4 hours, when the sodium completely dissolved and a red syrupy fluid was obtained. This was dissolved in ice water and the unaltered ester removed with ether. The aqueous solution was then acidified cold with hydrochloric acid and the free ketone ester extracted with ether. This was dried over calcium chloride and finally purified by distillation under diminished pressure. We obtained from 100 g. of ethyl  $\alpha$ -ethoxypropionate 80 g. of crude ester which yielded on distillation 30 g. of the pure ketone ester boiling at  $114^{\circ}$  under a pressure of 14 mm.

Calc. for  $C_{10}H_{18}O_4$ : C, 59.36, H, 8.91. Found: C, 58.74; H, 8.79.

**Ethyl  $\alpha$ -Methyl- $\gamma$ -methyl- $\gamma$ -methoxyacetoacetate**,  $CH_3CH(OCH_3).CO.CH(CH_3).COOC_2H_5$ .—This ester was prepared by condensation of ethyl propionate with ethyl  $\alpha$ -methoxypropionate in the presence of metallic sodium. The procedure was similar to that described above. The yield of pure distilled ester in this case was 36% of the theoretical. It boiled at  $105^{\circ}$  at 14 mm. pressure.

Calc. for  $C_{10}H_{18}O_4$ : C, 57.44; H, 8.51. Found: C, 56.90; H, 8.40.

**Ethyl  $\gamma$ -Ethoxy- $\gamma$ -methylacetoacetate**,  $CH_3CH(OC_2H_5).CO.CH_2.COOC_2H_5$ .—This ester has already been described by Chernoff<sup>1</sup> who prepared it by application of Reformatsky's reaction with ethyl chloroacetate and ethyl  $\alpha$ -ethoxypropionate. We find that the ester is more easily prepared and obtained in better yield by condensing the ethyl  $\alpha$ -ethoxypropionate with ethyl acetate in the presence of sodium. The following proportions were taken: 100 g. of ethyl  $\alpha$ -ethoxypropionate, 75 g. of ethylacetate and 17 g. of sodium. We obtained 65 g. of the  $\beta$ -ketone ester boiling at  $107^{\circ}$  at 16 mm. or a yield of ester corresponding to 58% of the theoretical. Chernoff assigned to his product the same boiling point but his yield was only 6.3% of theory. In another experiment we obtained, by condensation of 30 g. of ethyl  $\alpha$ -ethoxypropionate with 30 g. of ethyl acetate, 13.5 g. of the  $\beta$ -ketone ester.

**2-Thio-4( $\alpha$ -ethoxyethyl)-6-oxypyrimidine (XI).**—This new pyrimidine is easily obtained by condensation of ethyl  $\gamma$ -ethoxy- $\gamma$ -methylacetoacetate with thiourea. The description of a single experiment will illustrate our general procedure for preparing the compound. Seventeen grams of sodium were dissolved in 300 cc. of absolute alcohol and 40 g. of thiourea then dissolved in the ethylate solution. Sixty-five grams of the above  $\beta$ -ketone ester were then added and the mixture heated on a steam bath for about 10 hours. The sodium salt of the thiopyrimidine separated. The excess of alcohol was removed by evaporation at  $100^{\circ}$  and the residue

<sup>1</sup> Dissertation, Yale University, 1914.

dissolved in water. On acidifying this aqueous solution with hydrochloric acid the above pyrimidine separated as a colorless solid. It was purified by crystallization from hot water and separated as stout prisms melting at 206–208°. The yield was 40 g.

Calc. for  $C_8H_{12}O_2N_2S$ : N, 14.00. Found: N, 14.20.

**2,6-Dioxy-4( $\alpha$ -ethoxyethyl)pyrimidine (XII).**—This pyrimidine was easily obtained by desulfurization of the corresponding sulfur compound with chloroacetic acid. Thirty-six grams of the thiopyrimidine were digested with 31 g. of chloroacetic acid in 600 cc. of water for 10 hours. The solution was then evaporated to dryness at 100°, several additions of alcohol being made near the end of the operation to aid the removal of the chloroacetic acid by esterification. The residue was triturated with cold water and the insoluble pyrimidine purified by crystallization from hot water. It separated on cooling in the form of colorless, elongated prisms which melted at 184–186°. The yield was 20 g.

Calc. for  $C_8H_{12}O_3N_2$ : N, 15.22. Found: N, 15.19.

**2,6-Dioxy-4( $\alpha$ -ethoxyethyl)-5-bromopyrimidine (XIII).**—This compound was prepared by allowing an excess of bromine to interact, at ordinary temperature, with 2,6-dioxy-4( $\alpha$ -ethoxyethyl)-pyrimidine in acetic acid. After evaporating the acid and triturating the reaction product with water this bromo compound separated in a crystalline condition. It crystallized from boiling water in flat prisms melting at 206° to a clear oil. The pyrimidine is very soluble in alcohol.

Calc. for  $C_8H_{11}O_3N_2Br$ : N, 10.65. Found: N, 10.74.

**The Behavior of 2,6-Dioxy-4( $\alpha$ -ethoxyethyl)-pyrimidine on Hydrolysis with Acids:** *The Action of Hydrobromic Acid.*—An important result that really directed our procedure in hydrolyzing this pyrimidine was our observation that carbon dioxide was given off when this pyrimidine was digested with acids. In consequence of this unexpected behavior we were obliged to hydrolyze under specific conditions in order to obtain consistent results. The method of operating, which was finally adopted as the most successful, was as follows: Five grams of the pyrimidine and 25 cc. of hydrobromic acid were heated under a return condenser at 130° in an oil bath. It dissolved almost immediately on warming, with evolution of a gas which was identified as carbon dioxide. This effervescence was continuous for about 2 hours. During this transformation ethyl bromide was also given off and condensed in globules in the condenser tube. After the evolution of carbon dioxide ceased, the heating was continued for about 3 hours longer. The resulting fluid was dark red in color and on evaporating, to remove hydrobromic acid, a semi-solid residue was obtained. In order to remove the last trace of hydrobromic acid this was triturated with alcohol and the evaporation repeated. The residue was finally triturated with a small volume of cold water when

a colorless, granular substance deposited. This was separated and purified by crystallization from hot water. It deposited in the form of plates or distorted prisms which did not melt below  $300^{\circ}$ . More of the same compound was obtained when the original aqueous extract was neutralized with ammonia. In other words the substance was slightly basic, forming a hydrobromide which underwent dissociation on treatment with water. After final purification the product did not show a definite melting or decomposition point. It always began to turn brown when heated at  $280^{\circ}$  and remained in this condition at  $300^{\circ}$ . By repeated crystallization from hot water much material was lost as the compound appeared to undergo a change by such a treatment, being transformed into a more soluble product. What was formed here, we were unable to establish with the amount of material that was available for experimental purposes. The original compound was found to contain the same percentage of nitrogen as uracil. In fact uracil was the pyrimidine looked for here if the nucleoside underwent hydrolysis with formation of acetaldehyde and ethyl bromide. The compound was not, however, uracil. It was more soluble in water than uracil and did not respond to Wheeler and Johnson's test<sup>1</sup> for this combination. It also gave no test for bromine, proving that we were not dealing with a hydrobromic acid salt.

In another experiment 4 g. of the pyrimidine were digested with 20 cc. of hydrobromic acid for 7 hours and the excess of hydrobromic acid removed by heating on the steambath. The residue was then dissolved in 130 cc. of water, decolorized by digestion with bone coal and the solution finally cooled. One and five-tenths grams of the hydrolytic product separated. This did not melt at  $300^{\circ}$  and did not respond to the characteristic test for uracil. The aqueous solution was concentrated and cooled, when a thick syrup was obtained which gave a strong test for hydrobromic acid. This dissolved easily in cold water and on adding dilute sodium hydroxide solution a crystalline substance separated which was identified as the hydrolytic product described above. A trace of ammonia was also evolved when sodium hydroxide was added in excess. The weight obtained here was 1.3 g. This was purified by crystallization from water and showed no signs of melting at  $300^{\circ}$ . The average yield of the purified hydrolytic product was equivalent to about one-fifth of the weight of the nucleoside taken.

Calc. for  $C_8H_{12}ON_2$ : C, 53.56, H, 7.14; N, 25.00.

Found: C, 54.5, 53.56, 54.0; H, 6.85, 6.66, 7.17, 7.3, 7.00; N, 24.87, 24.86.

The reaction is expressed by the following equation:



*The Action of Hydriodic Acid.*—A preliminary experiment dealing with the behavior of 2,6-dioxy-4-( $\alpha$ -ethoxyethyl)-pyrimidine towards hy-

<sup>1</sup> *Loc. cit.*

driodic acid and phosphorus<sup>1</sup> was productive of results which indicated that this pyrimidine does not interact normally with this acid. Chernoff states that he did not obtain 4-ethyluracil, but a crystalline substance possessing entirely different properties. No analysis was made, but he states that the compound was purified by crystallization from water and did not melt at 280°. We have now investigated this reaction and find that the compound formed is identical with that produced by hydrolysis with hydrobromic acid. One gram of the ethoxypyrimidine was digested with 10 cc. of hydriodic acid at 140° for 3 hours. There was an evolution of carbon dioxide and ethyl iodide distilled from the solution. After completion of the reaction a little red phosphorus was introduced and the excess of acid removed by heating at 100°. A viscous residue was obtained which was dissolved in hot water, filtered and the solution allowed to cool slowly. Distorted prisms finally deposited. They turned brown when heated at 280° but did not melt at 300°. When this substance was mixed with that obtained by hydrolysis with hydrobromic acid and heated in a capillary tube there was no lowering of the melting point.

Calc. for  $C_8H_9ON_2$ : N, 25.00. Found: N, 25.1.

**Quantitative Determination of the Carbon Dioxide Evolved by Hydrolysis of 2,6-Dioxy-4( $\alpha$ -ethoxyethyl)-pyrimidine with Hydrobromic and Hydriodic Acids:** *Hydrolysis with Hydrobromic Acid.*—In order to determine quantitatively the amount of carbon dioxide given off during hydrolysis the operation was carried on in a specially constructed apparatus. Our procedure was to conduct a current of carbon dioxide-free air through the digestion flask (connected to a condenser) and lead it through a train of washing bulbs containing 1% hydrochloric acid, anhydrous calcium chloride and sulfuric acid. After this thorough washing, the gas mixture was then conducted through a weighed potassium hydroxide bulb where the carbon dioxide was absorbed and determined quantitatively. The analytical results obtained agreed very closely with that required by the equation given above, and were surprisingly constant when one takes into consideration that we are dealing here with a reaction which at best cannot be accurately controlled. They are in accord with the analytical values for carbon obtained by complete combustion.

2.1114, 1.3929 and 1.3962 g. pyrimidine gave 0.4809, 0.3372 and 0.2970 g.  $CO_2$ .

Calc. for one mol. of  $CO_2$  from  $C_8H_{12}O_3N_2$ :  $CO_2$ , 23.9. Found:  $CO_2$ , 22.8, 24.4 and 21.0.

*Hydrolysis with Hydriodic Acid.*—Carbon dioxide determination:

(4) 0.9936 g. pyrimidine gave 0.1970 g.  $CO_2$ .

Calc. for one mol.  $CO_2$  from  $C_8H_{12}O_3N_2$ :  $CO_2$ , 23.9. Found:  $CO_2$ , 20.0.

NEW HAVEN, CONN.

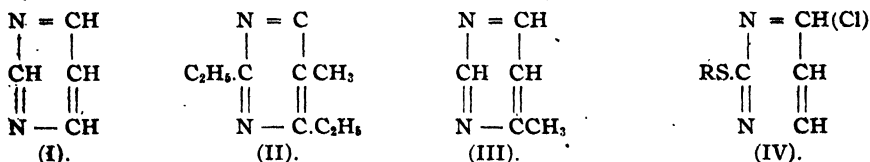
<sup>1</sup> Chernoff, Dissertation, Yale, 1914.

[CONTRIBUTIONS FROM THE SHEFFIELD CHEMICAL LABORATORY OF YALE UNIVERSITY.]  
**RESEARCHES ON PYRIMIDINES. LXXXII. THE SYNTHESIS OF  
 1,3-DIAMINES BY REDUCTION OF 2-MERCAPTO-  
 6-OXYPYRIMIDINES.<sup>1</sup>**

By TREAT B. JOHNSON AND A. WILLARD JOYCE.

Received July 7, 1916.

The first investigator to observe the formation of acyclic derivatives by the reduction of pyrimidines was apparently E. von Meyer.<sup>2</sup> In his early work on the determination of the constitution of "Kyanäthins," he investigated the action of sodium amalgam on 2,4-diethyl-5-methyl-6-aminopyrimidine (II), in acid solution, and showed that this pyrimidine underwent reduction with cleavage of the ring giving ammonia, propionic aldehyde and a basic oil of unknown constitution. The same products were also formed, according to him, by reduction of this pyrimidine with sodium and alcohol. So far as the writers are aware this work of von Meyer's has never been repeated and consequently the structure of this basic reduction product has never been established. The next investigator to observe a cleavage of the pyrimidine ring by reduction in alkaline solution was Byk<sup>3</sup> who reduced 4-methylpyrimidine with sodium and alcohol and showed that it was transformed into 1,3-diaminobutane. Recently, Johnson and Joyce<sup>4</sup> have contributed further data on this subject. They investigated the action of sodium and alcohol on 2-mercapto-6-chloropyrimidines and found that such combinations easily break down by reduction with the above reagents, forming 1,3-diamines.



In the light of these interesting results it was important to extend further our investigations and examine the behavior of mercaptooxypyrimidines towards alkaline reducing agents. Combinations of this type are more available than representatives of the above series and can be synthesized easily in quantity. The electrolytic reduction of oxypyrimidines has been applied with success by Tafel and his co-workers. According to these investigators 4-methyluracil<sup>5</sup> is reduced by electrolysis

<sup>1</sup> This paper and also that entitled "The Reduction of 2-Mercapto-6-chloropyrimidines" (THIS JOURNAL, 38, 1385 (1916)) were constructed from a dissertation presented by Asa Willard Joyce to the Faculty of the Graduate School of Yale University, 1916, in candidacy for the Degree of Doctor of Philosophy.

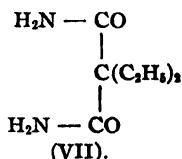
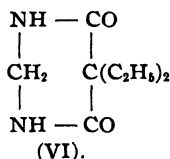
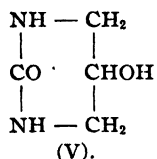
<sup>2</sup> *J. prakt. Chem.*, [2] 39, 262 (1889).

<sup>3</sup> *Ber.*, 36, 1917 (1903).

<sup>4</sup> THIS JOURNAL, 38, 1385 (1916).

<sup>5</sup> Tafel and Weinschenk, *Ber.*, 33, 3378 (1900).

in acid solution to methyltrimethylene urea, and with partial cleavage of the ring<sup>9</sup> forming diaminobutane,  $\text{NH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{NH}_2$ . Barbituric acid<sup>1</sup> gave by reduction under similar conditions hydouracil and trimethyleneurea. These same products were formed by reduction of dialuric acid<sup>2</sup> and also oxytrimethylene urea (V), while alloxan and uramil were transformed into hydouracil. 5-Ethylbarbituric acid<sup>3</sup> reacted in a similar manner as barbituric acid, giving 5-ethylhydouracil while *veronal* (5,5-diethylbarbituric acid) underwent an abnormal change and was converted into 5,5-diethyl-4,6-dioxyhexahydropyrimidine, (VI). Einhorn and Diesbach<sup>4</sup> have shown that 2-thio-5,5-diethylbarbituric acid is reduced by the action of sodium amalgam with cleavage of the pyrimidine ring forming diethylmalonamide (VII), formic acid and hydrogen sulfide. Veronal, on the other hand, was not reduced when subjected to similar conditions.



We have now investigated the action of sodium and alcohol on six 2-mercapto-6-oxypyrimidines and one 2-thio combination, namely:

- (1) 2-Methylmercapto-6-oxypyrimidine.<sup>5</sup>
- (2) 2-Ethylmercapto-5-ethoxy-6-oxypyrimidine.<sup>6</sup>
- (3) 2-Ethylmercapto-4-methyl-6-oxypyrimidine.<sup>7</sup>
- (4) 2-Ethylmercapto-5-methyl-6-oxypyrimidine.<sup>8</sup>
- (5) 2-Ethylmercapto-1-methyl-6-oxypyrimidine.<sup>9</sup>
- (6) 2-Ethylmercapto-1,4-dimethyl-6-oxypyrimidine and
- (7) 2-Thio-4-methyl-6-oxypyrimidine.<sup>10</sup>

All of these combinations have been described in the literature, with the single exception of 2-ethylmercapto-1,4-dimethyl-6-oxypyrimidine (6). This was prepared by alkylation of 2-ethylmercapto-4-methyl-6-oxypyrimidine with methyl iodide. Its structure was established by the fact that it underwent hydrolysis with concentrated hydrochloric acid giving 1,4-dimethyluracil<sup>11</sup> and ethyl mercaptan.

<sup>1</sup> Tafel and Weinschenk, *Loc. cit.*

<sup>2</sup> Tafel and Reindl, *Ber.*, **34**, 3286 (1901).

<sup>3</sup> Tafel and Thompson, *Ibid.*, **40**, 4489 (1907).

<sup>4</sup> *Ber.*, **40**, 4902 (1907).

<sup>5</sup> Wheeler and Merriam, *Am. Chem. J.*, **29**, 483 (1903).

<sup>6</sup> Johnson and McCollum, *J. Biol. Chem.*, **1**, 44 (1906).

<sup>7</sup> Johns, *Am. Chem. J.*, **40**, 351 (1908).

<sup>8</sup> Wheeler and Johnson, *Ibid.*, **31**, 595 (1904).

<sup>9</sup> Johnson and Heyl, *Ibid.*, **37**, 633 (1907).

<sup>10</sup> List, *Ann.*, **236**, 12 (1886).

<sup>11</sup> Johnson and Heyl, *Loc. cit.*

We now find that all of these seven pyrimidines are reduced smoothly by means of sodium and alcohol with formation of acyclic compounds. In other words, they undergo reduction with cleavage of the pyrimidine ring, giving their corresponding 1,3-diamines. These are as follows:

- (1) and (2) Trimethylenediamine,  $\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ .<sup>1</sup>
- (3) and (7) Diaminobutane,  $\text{NH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{NH}_2$ .<sup>2</sup>
- (4) 1,3-Diaminoisobutane,  $\text{NH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{NH}_2$ .
- (5) 1-Amino-3-methylaminopropane,  $\text{CH}_3\text{NH}\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ .
- (6) 1-Methylamino-3-aminobutane,  $\text{CH}_3\text{NH}\cdot\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)\cdot\text{NH}_2$ .

In no case were we able to isolate an intermediate mercapto derivative of a reduced pyrimidine. The constant evolution of mercaptan during the reaction indicated the instability of such combinations when formed. The reduction of this type of pyrimidine combinations with sodium and alcohol, therefore, affords a practical method for the synthesis of 1,3-diamines. Bases of this type should be of physiological and pharmacological interest, and our method of synthesis should make available new combinations which it would be very difficult to prepare by other known methods.

Attempts to synthesize the amino ether,  $\text{NH}_2\text{CH}_2\text{CH}(\text{OC}_2\text{H}_5)\text{CH}_2\text{NH}_2$ , by reduction of 2-ethylmercapto-5-ethoxy-6-oxypyrimidine were unsuccessful. In every experiment tried the ethoxy group ( $\cdot\text{OC}_2\text{H}_5$ ) was reduced and trimethylenediamine was the final product of the reaction. That the ethoxy group is destroyed by reduction with sodium has been observed in other cases. *o*-Ethoxybenzoic acid<sup>3</sup> reacts in a manner similar to that of our pyrimidine, when reduced with sodium and alcohol, giving hexahydrobenzoic acid. 1,4-Ethoxynaphthoic acid is also transformed by reduction with sodium amalgam into tetrahydro- $\alpha$ -naphthoic acid.<sup>4</sup>

The difficulty of obtaining mono-alkylated diamines is well known and, as far as the writers are aware, no alkyl derivatives of 1,3-diamines, containing alkyl groups linked to one or both nitrogen atoms are described in the literature. Our method of synthesis enables us to obtain such combinations without difficulty. The 2-mercapto-pyrimidines easily undergo alkylation, and by reduction of the resulting alkyl derivatives with sodium and alcohol the corresponding mono-alkylated diamines are formed. Dialkylated pyrimidines like 1,3-diethyluracil (VIII) theoretically should undergo reduction with formation of symmetrically substituted amines (IX).

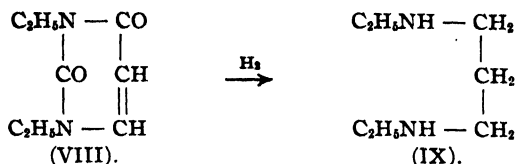
<sup>1</sup> Fischer and Koch, *Ber.*, 17, 1799 (1884); Gabriel and Wiener, *Ibid.*, 21, 2670 (1888).

<sup>2</sup> Byk, *Loc. cit.*; Tafel, *Ber.*, 33, 3382 (1900).

<sup>3</sup> Einhorn and Sumsden, *Ann.*, 286, 265 (1895).

<sup>4</sup> Kamm and McCluggage, *This Journal*, 38, 424 (1916).





This investigation will be continued in this laboratory.

### Experimental Part.

**The Reduction of 2-Methylmercapto-6-oxypyrimidine with Sodium and Alcohol. The Formation of Trimethylene Diamine,  $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2$ .**—The 2-methylmercapto-6-oxypyrimidine used in this experiment was prepared according to the method described by Wheeler and Merriam<sup>1</sup> by the condensation of pseudomethylthiourea hydriodide with the sodium salt of ethyl formylacetate. Twenty grams of sodium (2 molecular proportions) were placed in a liter flask, connected with dropping funnel and return condenser, and a solution of 10 g. of the pyrimidine in 200 cc. of absolute alcohol allowed to drop upon the sodium. If all the sodium failed to dissolve, after the addition of this solution, the mixture was heated on the steam bath and enough alcohol added to effect complete solution. During the operation methylmercaptan and ammonia were evolved and the solution assumed a dark, reddish brown color. After complete reduction air was blown through the mixture to expel as much ammonia as possible and the solution subjected to a steam distillation. Methylmercaptan distilled over with the trimethylene diamine. The distillate was conducted into hydrochloric acid solution, and after the operation was over, the acid solution was then concentrated by evaporation under diminished pressure. The diamine hydrochloride separated from the saturated solution as colorless, prismatic crystals. It was purified by crystallization from 25% alcohol and melted with decomposition at 243–245°. The yield was 5 g. or 47% of theory.

Calc. for  $\text{C}_3\text{H}_{10}\text{N}_2\cdot 2\text{HCl}$ : N, 19.04. Found: N, 19.04, 19.02.

**The Behavior of 2-Methylmercapto-6-oxypyrimidine towards Sodium Amalgam.**—Five grams of the oxypyrimidine and 2.0 g. of sodium hydroxide were dissolved in 50–100 cc. of water. One hundred and twelve grams of 3% sodium amalgam were then added in small amounts at a time, and the solution heated until there was no evolution of hydrogen gas. During this operation there was no evolution of mercaptan or ammonia indicating that the pyrimidine ring was not reduced. The aqueous solution did not give an alkaline distillate after steam distillation. After the steam distillation the alkaline solution was acidified with hydrochloric acid and cooled, when a colorless precipitate separated. This was filtered off and crystallized from hot water, from which it separated, on cooling, in glisten-

<sup>1</sup> *Loc. cit.*

ing plates. These melted at  $197-199^{\circ}$  and were identified as the unaltered mercaptopyrimidine. Three grams of the pyrimidine were recovered here. The filtrates were evaporated to dryness, and the residue digested with 75 cc. of absolute alcohol. This solution was filtered from inorganic salts and cooled when we recovered one gram more of the pyrimidine. In other words, the mercaptopyrimidine was not reduced by the amalgam.

**Reduction of 2-Ethylmercapto-5-ethoxy-6-oxypyrimidine.**—The pyrimidine used for reduction was prepared according to the method originally described by Johnson and McCollum.<sup>1</sup> Ten grams of the pyrimidine were taken for reduction and the operation conducted under similar conditions as described in the previous experiment. The base was removed as usual by steam distillation and obtained in the form of its hydrochloride. This crystallized from hot water in the form of needle-like prisms and melted at  $243-244^{\circ}$  with decomposition. The melting point of a mixture of this salt and the hydrochloride of trimethylene-diamine melted at  $243-244^{\circ}$  proving that the two were identical. The yield of this salt in this case was 3.0 g. or 40% of theory.

Calc. for  $C_8H_{10}N_2 \cdot 2HCl$ : N, 19.04. Found: N, 19.2.

**Reduction of 2-Ethylmercapto-4-methyl-6-oxypyrimidine. The Formation of 1,3-Diaminobutane,  $CH_3 \cdot CH \cdot CH_2 \cdot CH_2 \cdot NH_2$ .**—The 2-ethyl-



mercapto-4-methyl-6-oxypyrimidine used was prepared according to the directions of Johns<sup>1</sup> by condensing pseudoethylthiourea with the sodium salt of ethyl acetoacetate. Fifteen grams were taken for reduction and the operation carried out as described in the previous experiments. Since difficulty was encountered in accomplishing a separation of the hydrochloride of the base from ammonium chloride, the mixture of the two salts was treated with a 30% solution of sodium hydroxide when the amine separated as an oil. Air was blown through the mixture to expel ammonia, and the diamine extracted with ether and dried over potassium hydroxide. The ether solution was then saturated with carbon dioxide when the carbonate of the diamine separated. This was filtered out and decomposed by treatment with an alcoholic solution of hydrochloric acid. The hydrochloride separated in the form of hexagonal prisms melting at  $169-170^{\circ}$ . According to Byk<sup>1</sup> the hydrochloride of this base melts at  $167^{\circ}$ . Tafel<sup>1</sup> assigned to it a melting point of  $170-172^{\circ}$ . The yield was 6.2 g. or 65% of the theoretical.

Calc. for  $C_4H_{12}N_2 \cdot 2HCl$ : N, 17.37. Found: N, 17.37, 17.34.

**Reduction of 2-Ethylmercapto-5-methyl-6-oxypyrimidine. The Formation of 1,3-Diaminoisobutane,  $NH_2 \cdot CH_2 \cdot CH(CH_3) \cdot CH_2 \cdot NH_2$ .**—The 2-ethylmercapto-5-methyl-6-oxypyrimidine was prepared according to the

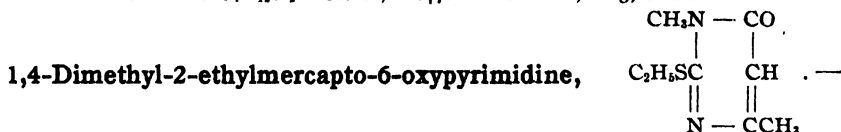
<sup>1</sup> *Loc. cit.*

method described by Wheeler and Johnson.<sup>1</sup> Ten grams of the pyrimidine were used for reduction. The hydrochloride of the 1,3-diaminoisobutane was purified by crystallization from absolute alcohol and separated in the form of needles. They melted at 196° to a colorless oil. About 3 g. of this salt dissolves in 200–225 cc. of boiling absolute alcohol. The yield was 5 g. or 52% of theory.

Calc. for  $C_4H_{12}N_2 \cdot 2HCl$ : N, 17.37. Found: N, 17.43, 17.50.

**Reduction of 1-Methyl-2-ethylmercapto-6-oxypyrimidine. The Formation of 1-Amino-3-methylaminopropane,  $CH_3NH \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot NH_2$ .**—The 1-methyl-2-ethylmercapto-6-oxypyrimidine was prepared by the alkylation of 2-ethylmercapto-6-oxypyrimidine<sup>2</sup> with methyl iodide. The reduction was carried on as described above but in this case we obtained a poorer yield of the base. We also encountered difficulty in separating the hydrochloride from ammonium chloride. This was accomplished by repeated crystallizations from absolute alcohol and was obtained in the form of colorless plates which melted at 185–190° to an oil. The yield of crude salt was 37% of theory.

Calc. for  $C_4H_{12}N_2 \cdot HCl$ : N, 22.47. Found: N, 22.3, 22.21.



Thirty grams of 2-ethylmercapto-4-methyl-6-oxypyrimidine were dissolved in 100 cc. of an alcoholic solution containing 10 g. of potassium hydroxide. The pyrimidine dissolved readily. After cooling, 30 g. of methyl iodide were added and the mixture warmed gently until it gave no alkaline reaction. After filtering off potassium iodide the excess of alcohol was evaporated when an oil was obtained. This was extracted with ether and dried over anhydrous sodium sulfate. Calcium chloride could not be used as a drying agent as it combined with the pyrimidine. The yield was 17.2 g. This pyrimidine was purified by crystallization from ether and deposited in the form of prisms which melted at 63–64° to a clear oil. The compound is soluble in ether, benzene and alcohol and insoluble in water, alkalis and acid solutions.

Calc. for  $C_8H_{12}ON_2S$ : N, 15.21. Found: N, 15.15, 15.24.

The structure of this pyrimidine was established by its behavior on hydrolysis. When digested with concentrated hydrochloric acid ethylmercaptan was evolved and 2-oxy-1,4-dimethylpyrimidine was formed, melting at 260°.<sup>1</sup>

**Reduction of 1,4-Dimethyl-2-ethylmercapto-6-oxypyrimidine. The Formation of 1-Methylamino-3-aminobutane,  $CH_3NH \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot NH_2$ .**

<sup>1</sup> *Loc. cit.*

<sup>2</sup> Johnson and Heyl, *Ibid.*

$(\text{CH}_3)_2\text{NH}_2$ .—This transformation was accomplished by reduction with sodium and alcohol. The hydrochloride of the diamine was obtained in the form of plates melting at  $223^\circ$ . It was purified by crystallization from absolute alcohol. The salt is very soluble in water, moderately soluble in absolute alcohol and insoluble in ether and benzene.

Calc. for  $\text{C}_8\text{H}_{14}\text{N}_2\cdot\text{HCl}$ : N, 20.2. Found: N, 20.5, 20.2.

**Reduction of 2-Thio-4-methyl-6-oxypyrimidine. The Formation of 1,3-Diaminobutane,  $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{CH}_3)\cdot\text{NH}_2$ .**—The thiopyrimidine was prepared according to the directions of List.<sup>1</sup> Five grams of the pyrimidine were suspended in 100 cc. of absolute alcohol and 20 g. of sodium gradually added. Ammonia was evolved and 150 cc. of alcohol were finally added to complete the solution of the sodium. The amine was removed by distillation with steam and converted into its hydrochloride. We obtained 1.9 g. of the salt melting at  $165$ – $167^\circ$ . A mixture of this with some pure hydrochloride of 1,3-diaminobutane melted at the same temperature. The hot alkaline solution remaining after the steam distillation was filtered and neutralized with hydrochloric acid. On cooling, 2 g. of unaltered 2-thio-4-methyluracil were recovered.

**Diurea of 1,3-Diaminobutane,  $\text{NH}_2\text{CONH}\cdot\text{CH}_2\cdot\text{CH}(\text{CH}_3)\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ .**—One-half gram of the hydrochloride of 1,3-diaminoisobutane was dissolved in 10 cc. of water and one gram of silver cyanate added. The mixture was then digested on the steam bath for 15–20 minutes and the silver chloride separated by filtration.\* The urea was obtained by evaporation to dryness and purified by crystallization from alcohol. It separated in the form of clusters of distorted needles melting at  $172^\circ$ .

Calc. for  $\text{C}_6\text{H}_{14}\text{O}_2\text{N}_4$ : N, 32.16. Found: N, 32.09.

**Picrate of 1,3-Diaminobutane.**—This salt crystallizes from hot water in the form of yellow needles which melt at  $240$ – $245^\circ$  with decomposition.

Calc. for  $\text{C}_4\text{H}_{12}\text{N}_2(\text{C}_6\text{H}_3\text{O}_7\text{N}_3)_2$ : N, 20.51. Found: N, 20.24.

NEW HAVEN, CONN.

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[CONTRIBUTIONS FROM THE SHEFFIELD CHEMICAL LABORATORY OF YALE UNIVERSITY.]  
**RESEARCHES ON THIOCYANATES AND ISOTHIOCYANATES. X.  
 THE UTILIZATION OF TETRACHLOROMETHYLMER-  
 CAPTAN FOR THE PREPARATION OF  
 ALKYL ISOTHIOCYANATES.<sup>2</sup>**

BY TREAT B. JOHNSON AND E. HEATON HEMINGWAY.

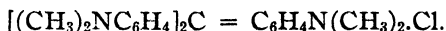
Received July 7, 1916.

Tetrachloromethylmercaptan VI, and amines combine to give representatives of an interesting class of compounds which have not been

<sup>1</sup> *Loc. cit.*

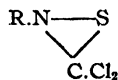
<sup>2</sup> This paper and also that entitled "Ethyl Isothiocyanacetate" (THIS JOURNAL, 38, 1550) were constructed from a dissertation presented by Earl Heaton Hemingway to the Faculty of the Graduate School of Yale University, 1916, in candidacy for the Degree of Doctor of Philosophy.

very thoroughly investigated. The chlorine attached to sulfur is the reactive halogen atom of the mercaptan, and is removed by the action of amines, giving hydrochloric acid and almost quantitative yields of sulfamides. The anilide represented by Formula VII, is a representative of the type of compounds formed. This reaction was discovered by Rathke<sup>1</sup> in 1870 and later applied by him successfully for the preparation of the sulfanilide, VII, and the corresponding *o*- and *p*-sulfotoluides. No analyses, however, were reported. With dimethylaniline, tetrachloromethylmercaptan interacts with formation of methylviolet,<sup>2</sup>

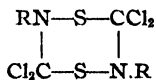


This process was patented in 1885<sup>3</sup> and the reaction applied with eleven different tertiary amines.

According to Rathke the sulfur combinations represented by Formula VII, are characterized by their behavior on heating and their action on alkalis. When subjected to the action of potash in alcoholic solution they lose a molecule of hydrochloric acid and are converted smoothly into unstable substances whose structure has never been established with certainty. Rathke suggested the two Formulas I and II, while Beilstein<sup>4</sup> expresses the constitution of these compounds according to both Formulas I and III. The second characteristic reaction is that which



(I).



(II).



(III).

takes place by application of heat. Under such conditions Rathke states that the sulfanilides break down with formation of volatile products and sulfur combinations possessing the odor of mustard oils. These latter compounds were never identified by him and, so far as we are aware, no one has established experimentally the correctness of Rathke's assumptions. The primary object of our work was to reinvestigate this reaction and determine whether sulfanilides actually undergo such an unique rearrangement.

The three sulfanilides described by Rathke were prepared by us and the sulfanilide, (VII), and *o*-sulfotoluide obtained as oils, which refused to solidify. The *p*-sulfotoluide was a solid which could be purified by crystallization without decomposition. We now find that all three of these compounds are exceedingly unstable and break down, when heated at

<sup>1</sup> *Ber.*, 3, 858 (1870); 19, 395 (1886); *Ann.*, 167, 211 (1873); *Zentralblatt*, 1872, 547.

<sup>2</sup> Rathke, *Ber.*, 19, 397 (1886).

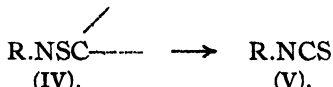
<sup>3</sup> *Farbenfabriken vorm Bayer and Co.*, *Ber.*, 18, Ref. 679; *R. P.*, 32,829 (1885); *Wagner's Chem. Tech.*, 31, 498 (1885).

<sup>4</sup> Vol. II, 426, 468, 504.

130–140°, with formation respectively, of two characteristic sulfur derivatives, namely, a *mustard oil*, (XII), and apparently a polymeric modification of the mustard oil, which we have represented provisionally by Formula XI. These latter products were obtained as brown, amorphous powders, which were practically insoluble in the common solvents. It is not improbable that the polymeric modification of benzoylisothiocyanate,  $C_6H_5CONCS$ , which was first described by Miquel,<sup>1</sup> is a representative of the same type of compounds and is to be represented by Formula X. Miquel writes as follows regarding this compound:

“Dersèche à l'étuve à 100 degrés, cette substance se présente sous la forme d'une poudre jaune amorphe, insipide d'une odeur faible et aromatique.”

In the case of *p*-sulfatoluide we obtained by heating this substance at 140° a yield of *p*-tolylisothiocyanate corresponding to 33% of the theoretical. In other words, we are dealing here with an unique rearrangement involving a transformation of the sulfide grouping IV, into that corresponding to a mustard oil (V).



So far as the writer is aware, combinations containing the unsaturated radical—NSC have never been prepared.

Our observation that a mustard oil (XII) is formed along with its corresponding polymeric modification (XI),\* when sulfanilides are heated, furnishes ample justification for certain assumptions regarding the mechanism of this interesting transformation. In the first place it seems probable that the change involves the formation of an unstable, intermediate compound which is highly unsaturated and secondly, that this combination is capable of transformation into either one of the end products of the reaction. Since this rearrangement involves a dissociation of the grouping —N.C.S— between S and N and a coupling of the N with C, it is evident that the intermediate compound must be cyclic in character.

The simplest expression which meets these conditions is that represented by the cycle (VIII). This compound is the same product that is formed by the interaction of a sulfanilide (VII) with alkali. An intermediate combination of this structure would be expected to be unstable at high temperatures and break down into chlorine and the free radical (IX). This then could undergo theoretically two fundamental changes, namely, either condense as a true methylene compound ( $CH_2=$ ) giving the polymer (XI), or undergo transformation directly into a mustard oil (XII) with rupture of the linking between nitrogen and sulfur. Such an explanation seems logical and the various changes are expressed by the following formulas:

<sup>1</sup> *Ann. chim. phys.*, [5] 11, 303 (1877).



### Experimental Part.

**The Action of Aromatic Amines on Tetrachloromethylmercaptan.**—According to Rathke,<sup>1</sup> tetrachloromethylmercaptan interacts with aniline, *p*- and *o*-toluidine at low temperature with formation of sulfanilides. The aniline and *o*-toluidine compounds were obtained as



oils and the *p*-toluidide described as a solid. No attempt was made to purify the compounds, however, and no analytical data were given confirming their constitution.

We have prepared these three compounds according to a common procedure which was as follows: Thirty grams of the tetrachloromethylmercaptan were dissolved in 300 cc. of ether and the mixture cooled with ice-water. Two molecular proportions of aniline (or the toluidines) were then slowly added and the mixture agitated after each addition. Aniline hydrochloride separated at once and the ether assumed a red color. After the final addition of the amine the mixture was then allowed to stand at ordinary temperature for one hour and the aniline hydrochloride separated by filtration. The ether solution was then dried over calcium chloride and the solvent finally allowed to evaporate spontaneously. When aniline was used we obtained 33 g. of the *trichloromethylsulfanilide*,  $\text{Cl}_3\text{C.SNHC}_6\text{H}_5$ , or 85% of a theoretical yield. This compound was obtained as an oil which did not solidify on standing. It cannot be purified by distillation. *Trichloromethyl-o-sulfotoluide*,  $\text{Cl}_3\text{CSNHC}_6\text{H}_4\text{CH}_3$ , was prepared and also obtained as an oil which could not be distilled without decomposition. The yield in this case was 87% of the theoretical.

**Trichloromethyl-*p*-sulfotoluide**,  $\text{Cl}_3\text{C.S.NHC}_6\text{H}_4\text{CH}_3$ .—From 40 g. of *p*-toluidine and 35 g. of tetrachloromethylmercaptan we obtained 47 g. of this sulfotoluide. It was purified by crystallization from petroleum ether and separated in the form of colorless crystals which melted at 72° to a yellow oil. At 145° this toluide decomposes with violent effervescence.

Calc. for  $\text{C}_8\text{H}_8\text{NSCl}_3$ : N, 5.4. Found: Kjeldahl, N, 5.21, 5.22.

**The Action of Alcoholic Potassium Hydroxide on Trichloromethylsulfanilides: Cyclic Dichloromethylenephénylimidosulfide (VIII).**—This sulfide has been described by Rathke<sup>2</sup> and its constitution established by a complete analysis. It was prepared by adding an alcoholic solution of potassium hydroxide to a cold ether solution of trichloromethylsulfanilide and separated in the form of prisms melting at 140°.

**Cyclic Dichloromethylene-*p*-tolylimidosulfide.**—This compound was prepared as follows: Five grams of trichloromethyl-*p*-sulfotoluide were

<sup>1</sup> *Loc. cit.*

<sup>2</sup> *Ber.*, 19, 395 (1886).



dissolved in ether and 1 g. of potassium hydroxide (one molecular proportion) added in alcoholic solution. Each drop of alkali added produced a deep red color which disappeared on shaking and potassium chloride deposited. After filtering from potassium chloride the ethereal solution was allowed to partly evaporate spontaneously and finally absolute alcohol was added to the residue, when this cyclic sulfide was precipitated. It was purified by crystallization from ether and separated in the form of colorless needles which decomposed with explosive violence when heated at  $145^{\circ}$ . This compound is soluble in alcohol and can be crystallized from this solvent without decomposition. On long digestion, however, it is gradually decomposed. Rathke<sup>1</sup> prepared this compound, but assigned to it a melting point of  $138^{\circ}$ . He did not report an analysis of his product.

Calc. for  $C_8H_7NSCl_2$ : N, 6.36. Found: N, 6.26, 6.00.

**Cyclic Dichloromethylene-*o*-tolylimidosulfide.**—This was obtained from trichloromethyl-*o*-sulftoluide by the action of potassium hydroxide. It was obtained as a solid and crystallized from ether in the form of prismatic blocks, which melted at  $112^{\circ}$  to an oil. At  $145^{\circ}$  the compound decomposes with violent evolution of gas.

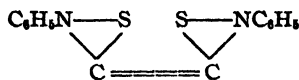
Calc. for  $C_8H_7NSCl_2$ : N, 6.3. Found: N, 5.90, 5.89.

**The Behavior of Trichloromethylsulfanilides on Heating. The Formation of Phenylisothiocyanate from Trichloromethylsulfanilide,  $Cl_3CS.NHC_6H_5 \rightarrow C_6H_5NCS$ .**—Thirty-three grams of trichloromethylsulfanilide were heated in an oil bath at  $125$ – $130^{\circ}$  for one hour. Hydrochloric acid was evolved and the sulfanilide was transformed into a brown colored resinous mass impregnated with oil. This was subjected to a steam distillation and the operation continued as long as oil distilled over. After the operation was complete, this oil was dissolved in ether and dried over calcium chloride. On evaporating the ether we obtained 3.0 g. of phenylmustard oil. When this was combined with the required amount of aniline they interacted with evolution of heat, giving quantitatively symmetrical diphenylthiourea melting at  $153^{\circ}$ . A mixture of this compound and diphenylthiourea melted at the same temperature. The water solution, which collected during the distillation, was filtered from a brown solid left behind in the flask and evaporated to dryness. From this we obtained 2.5 g. of aniline hydrochloride.

The brown residue, which was insoluble in water, was dried and weighed 12 g. It was purified by washing several times with boiling ether to remove traces of oil and then dried for analysis at  $80^{\circ}$ . The compound was insoluble in all the common organic solvents and responded to a test for sulfur. It did not contain chlorine. When heated in a capillary tube it fused to a tar at  $140^{\circ}$  and then began to decompose as

<sup>1</sup> *Loc. cit.*

the temperature was raised. A nitrogen determination agreed with the calculated value for phenylisothiocyanate. Whether the following formula represents the structure of this interesting combination remains to be established.



Calc. for  $(\text{C}_7\text{H}_5\text{NS})$ : N, 10.37. Found: N, 10.37, 10.21.

**The Formation of *p*-Tolylisothiocyanate from Trichloromethylsulf-*p*-toluide,**  $\text{Cl}_3\text{CSNHC}_6\text{H}_4\text{CH}_3 \rightarrow \text{CH}_3\text{C}_6\text{H}_4\text{NCS}$ .—Forty-seven grams of trichloromethylsulf-*p*-toluide were decomposed by heating for one hour at  $110\text{--}120^\circ$ . The same process of purification was then applied as in the previous preparation when *p*-tolylisothiocyanate distilled over with the steam. We obtained 9.1 g. of this reagent, corresponding to  $33\frac{1}{3}\%$  of a theoretical yield. It boiled at  $234\text{--}238^\circ$  and combined with aniline forming symmetrical phenyl-*p*-tolylthiourea,  $\text{C}_6\text{H}_5\text{NHCSNHC}_6\text{H}_4\text{CH}_3$ .<sup>1</sup> It was purified by crystallization from alcohol and melted at  $143^\circ$ .

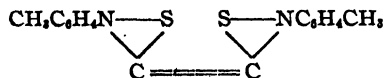
Calc. for  $\text{C}_{14}\text{H}_{14}\text{N}_2\text{S}$ : N, 11.57. Found: N, 11.57, 11.36.

The mustard oil was also combined with *p*-toluidine, when we obtained *sym*-ditolylthiourea<sup>2</sup> melting at  $181^\circ$ .

Calc. for  $\text{C}_{16}\text{H}_{16}\text{N}_2\text{S}$ : N, 10.95. Found: N, 10.70.

After steam distillation of the *p*-tolylisothiocyanate (above) a brown solid remained behind suspended in the water. This was separated by filtration and the aqueous solution evaporated to dryness, when we recovered 7.0 g. of *p*-toluidine hydrochloride.

The brown solid was ground to a fine powder, extracted thoroughly with ether and dried at  $100^\circ$ . It showed no signs of melting at  $270^\circ$  and was insoluble in the common solvents. A nitrogen determination indicated that we were dealing with a polymeric modification of *p*-tolylisothiocyanate.



Calc. for  $(\text{C}_8\text{H}_7\text{NS})$ : N, 9.4. Found: N, 9.0, 8.95.

**The Formation of *o*-Tolylisothiocyanate from Trichloromethylsulf-*o*-toluide,**  $\text{Cl}_3\text{CSNHC}_6\text{H}_4\text{CH}_3 \rightarrow \text{CH}_3\text{C}_6\text{H}_4\text{NCS}$ .—The decomposition of this toluide was effected by heating 19 g. of the compound for several hours at  $128^\circ$ . The very black residue which was obtained was then blown with steam as described in the two previous experiments. We obtained by this operation 3.0 g. of *o*-tolylisothiocyanate. The structure was established by the behavior of the oil towards aniline. They interacted at ordinary temperature with evolution of heat, giving *sym*-phenyl-*o*-

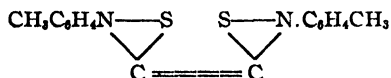
<sup>1</sup> Gebhardt, *Ber.*, 18, 3035 (1884).

<sup>2</sup> Maly, *Jahresbericht*, 1869, 637.

tolyl thiourea. This was purified by crystallization from alcohol and melted at 140–141°.<sup>1</sup>

**The Formation of *p*-Tolylisothiocyanate from Cyclic Dichloromethylene-*p*-tolylimidosulfide,**  $\text{CH}_3\text{C}_6\text{H}_4\text{N} \begin{array}{c} \diagup \text{S} \diagdown \\ \text{CCl}_2 \end{array} \rightarrow \text{CH}_3\text{C}_6\text{H}_4\text{NCS}$ .—The cyclic

sulfide is so explosive when heated to its melting point 145° that it is unsafe to decompose more than very small quantities at a time. Volumes of irritable gases containing chlorine are given off and a brown colored residue is left behind. Five grams of the sulfide were decomposed by heating in an oil bath at 140–145°. After the violent reaction had subsided and the mixture was cool, the residue was pulverized finely and thoroughly washed with ether and water. The ether solution was saved. The brown product was insoluble in all common organic solvents and did not melt at 270°. It was apparently identical with the product obtained by heating trichloromethylsulf-*p*-toluide. It was dried at 90°. Nitrogen determinations agreed with the calculated value for a polymer of *p*-tolylisothiocyanate. The compound contained sulfur but did not give a test for chlorine.



Calc. for  $(\text{C}_7\text{H}_7\text{NS})$ : N, 9.4. Found: N, 9.51, 9.50.

The ether solution obtained above was evaporated, when a small amount of oil was obtained which was *p*-tolylisothiocyanate. We did not obtain enough of this oil for distillation. When mixed with a few drops of aniline and the mixture warmed, there was an evolution of heat and a crystalline product formed which melted at 140–142°. It was identified as phenyl-*p*-tolylthiourea.

NEW HAVEN, CONN.

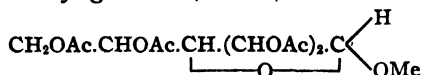
[CONTRIBUTION FROM THE CARBOHYDRATE LABORATORY, BUREAU OF CHEMISTRY,  
UNITED STATES DEPARTMENT OF AGRICULTURE.]

## THE OPTICAL ROTATORY POWERS OF SOME ACETYLATED DERIVATIVES OF MALTOSE, CELLOSE AND LACTOSE.

By C. S. HUDSON AND RALPH SAYRE.

Received July 8, 1916.

**The Rotatory Powers of the  $\beta$ -Heptacetates of Methyl Maltoside and Methyl Celloside.**—If the molecular rotations of the alpha and beta forms of tetracetyl methyl glucoside,



are denoted by  $(A + B)$  and  $(-A + B)$ ,<sup>2</sup> respectively, the molecular

<sup>1</sup> Hugershoff, *Ber.*, 36, 1141 (1903).

<sup>2</sup> Hudson and Dale, *THIS JOURNAL*, 37, 1264 (1915).

rotations of the alpha and beta forms of heptacetyl methyl maltoside may be expressed as  $(A + B')$  and  $(-A + B')$ , respectively, where  $A$  represents the rotation that is due to the terminal asymmetric carbon atom and  $B$  or  $B'$  that due to the remainder of the corresponding structures. The difference of the rotations of the alpha and beta forms of the acetylated glucosides is  $2A$ , and it has been shown in the article cited that this value is  $+53900$ , hence  $A = +26950$ . If the value of  $B'$  were known it should be possible, knowing  $A$ , to calculate the rotations of the two forms of heptacetyl methyl maltoside. A value for  $B'$  can be obtained from the observed molecular rotations of the alpha and beta forms of maltose octacetate, since this substance differs in structure from acetylated methyl maltoside only in respect to the terminal asymmetric carbon atom, which has the acetyl group in place of the methyl. The rotations of the two forms of the octacetate may accordingly be expressed as  $(A' + B')$  and  $(-A' + B')$  and their sum is  $2B'$ , which has been found to be  $+125400$ ,<sup>1</sup> or  $B' = +62700$ . Hence the specific rotation of alpha heptacetyl methyl maltoside (M. W. 650) is calculated to be  $(+26950 + 62700)/650 = +138^\circ$ , and that of the beta modification  $(-26950 + 62700)/650 = +55^\circ$ . Fischer and Armstrong<sup>2</sup> have prepared from the action of silver carbonate upon acetochloromaltose in methyl alcoholic solution a crystalline heptacetyl methyl maltoside, of m. p.  $121-122^\circ$ , but they have not recorded its rotation. By the same method Foerg<sup>3</sup> prepared the same substance, found it to melt at  $125-127^\circ$ , but did not record its rotation. Koenigs and Knorr<sup>4</sup> prepared from acetonitromaltose in methyl alcoholic solution by the action of barium carbonate and a trace of pyridine, a heptacetyl methyl maltoside of m. p.  $128-129^\circ$  and specific rotation in benzene  $+61^\circ$ . Judging from the values of the melting points, the substances are identical and probably consist of the beta form, because the acetohalogen sugar derivatives yield in general the glucosides of that series. The nearness of the recorded rotation in benzene ( $+61^\circ$ ) to that calculated for the beta modification in chloroform ( $+55^\circ$ ) also supports this conclusion, but we have considered it necessary to prepare the substance anew in order that its rotation in chloroform might be measured. The value which we find in this solvent is  $+54^\circ$ , which agrees almost exactly with the calculated rotation and proves clearly that the substance is the beta form of heptacetyl methyl maltoside. While no method is known for preparing the alpha modification, the agreement between calculation and experiment in the case of the beta form makes it very probable that the calculated value for the alpha form is not far from correct.

<sup>1</sup> Hudson and Johnson, *THIS JOURNAL*, 37, 1277 (1915).

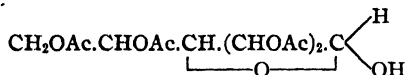
<sup>2</sup> *Ber.*, 34, 2895 (1901).

<sup>3</sup> *Monatsh.*, 23, 48 (1902).

<sup>4</sup> *Ber.*, 34, 4344 (1901).

By precisely similar calculation the rotations of the alpha and beta forms of heptacetyl methyl celloside may be calculated, the rotation of the acetylated cellose chain B" being obtained from the rotations of the alpha and beta forms of cellose octacetate. It has been found that B" = +8800,<sup>1</sup> hence the specific rotation of alpha heptacetyl methyl celloside (M. W. 650) is written  $(+26950 + 8800)/650 = +56^\circ$  and that of the beta form  $(-26950 + 8800)/650 = -28^\circ$ . Skraup and Koenigs<sup>2</sup> have prepared from acetochlorocellose in methyl alcoholic solution by the action of silver carbonate a heptacetyl methyl celloside which melted at  $173^\circ$ , but its rotation is not recorded. We have prepared this substance in pure condition and find it to melt at  $187^\circ$  (uncorr.) and to show the specific rotation in chloroform of  $-25.4^\circ$ , which is in good agreement with the calculated value for  $\beta$ -heptacetyl methyl celloside.

**The Rotatory Powers of the  $\beta$ -Heptacetates of Maltose, Cellose and Lactose.**—If the alpha and beta forms of glucose tetracetate,



were known, it should be possible to obtain from the difference of their molecular rotations the value of the rotatory power of the end asymmetric carbon atom, and by combining this value with those for the acetylated maltose, cellose or lactose chains, to obtain the rotations of the respective heptacetates of these biose sugars. These calculations would be entirely similar in method to those just indicated. Since the alpha form of glucose tetracetate has not been described, it is necessary to base the calculations upon some other similar pair of derivatives, and we have selected the alpha<sup>3</sup> and beta<sup>4</sup> tetracetates of galactose, which have recently been carefully purified in this laboratory, and their rotations in chloroform found to be  $+141^\circ$  and  $+22^\circ$ .<sup>5</sup> If the rotation of their end asymmetric carbon atom be written A" and that of the acetylated galactose residue B", the molecular rotation (M. W. 348) for the alpha form is  $(A'' + B'')$ , for the beta  $(-A'' + B'')$ , and the difference is  $2A''$ ,  $(141 - 22)348 = +41400$ , hence  $A'' = +20700$ . Using this value, the specific rotation of alpha maltose heptacetate (M. W. 636) is calculated to be  $(+20700 + 62700)/636 = +131^\circ$ , while that of the beta modification becomes  $(-20700 + 62700)/636 = +66^\circ$ . E. and H. Fischer<sup>6</sup> prepared the beta form from acetochloromaltose and record its melting point as  $179-180^\circ$

<sup>1</sup> Hudson and Johnson, *THIS JOURNAL*, **37**, 1278 (1915).

<sup>2</sup> *Monatsh.*, **22**, 1034 (1901).

<sup>3</sup> Skraup and Kremann, *Ibid.*, **22**, 1045 (1901).

<sup>4</sup> Unna, *Inaugural Diss.*, Berlin, 1911, p. 2.

<sup>5</sup> Hudson and Yanovsky, forthcoming publication. See *THIS JOURNAL*, **38**, 1226-1227 (1916).

<sup>6</sup> *Ber.*, **43**, 2523 (1910).

(corr.) and its initial specific rotation in acetylene tetrachloride  $+72.6^\circ$ , rising slowly to  $76.7^\circ$ . The rise is probably due to the slow establishment in solution of equilibrium between the alpha and beta forms by the mutarotation reaction. We have prepared and purified this beta form in order to measure its rotation in chloroform. The initial product showed  $[\alpha]_D = +78^\circ$  in this solvent, but on successive recrystallizations of the material from chloroform and ether, the value slowly fell; and only after sixteen recrystallizations did it become constant, indicating that the material was the pure beta form. The specific rotation of the pure substance was  $+67.8^\circ$  in chloroform, which agrees well with the calculated value for  $\beta$ -maltose heptacetate.

The specific rotations of the alpha and beta heptacetates of cellose may be calculated in the same manner from the data already mentioned to be  $(+20700 + 8800)/636 = +46^\circ$  for the alpha and  $(-20700 + 8800)/636 = -19^\circ$  for the beta modification. The cellose heptacetate which Fischer and Zemplen<sup>1</sup> prepared from iodo-acetyl cellose melted at  $195-197^\circ$  and showed  $[\alpha]_D = 20^\circ$  in chloroform. We have prepared this substance from acetobromocellose, and obtained  $+18^\circ$  for the rotation of the crude substance; but on crystallization the value gradually became lower without, however, becoming constant before the supply of material was exhausted. After eighteen recrystallizations the value was  $-2^\circ$ , which is  $17^\circ$  from the calculated value, but it seems reasonable to suppose that further purification would bring the values nearer.

The specific rotations of the alpha and beta forms of lactose heptacetate may be calculated from  $A'' = +20700$  and  $B'' = +16600$ , which is the value for one-half the sum of the molecular rotations of the alpha and beta octacetates of lactose,<sup>2</sup> to be  $(+20700 + 16600)/636 = +59^\circ$  for the alpha, and  $(-20700 + 16600)/636 = -6^\circ$  for the beta form. We have prepared lactose heptacetate, which does not appear to have been crystallized previously, by the action of silver carbonate on acetobromolactose in acetone solution. As in the case of cellose heptacetate, the amount of material available was not sufficient for completely purifying the beta form. The crude product, rotating  $+12^\circ$  in chloroform, was recrystallized twenty times, yielding a substance of rotation  $-0.3^\circ$  in chloroform, which is about  $6^\circ$  higher than that calculated for  $\beta$ -lactose heptacetate. Since the rotation has not yet reached a constant value, it is to be supposed that further purification would have made the agreement closer.

#### Experimental.

**Purification of Heptacetyl Methyl Maltoside.**—The acetobromomaltose used was prepared by the method of Dale,<sup>3</sup> which consists in treat-

<sup>1</sup> *Ber.*, 43, 2539 (1910).

<sup>2</sup> Hudson and Johnson, *This Journal*, 37, 1270 (1915).

<sup>3</sup> *This Journal*, 37, 2745 (1915).

ing the sugar with a saturated solution of hydrobromic acid in acetic anhydride. The compound could not be made to crystallize, but the amorphous sirup obtained by adding petroleum ether to its chloroform solution was sufficiently pure for our purpose. The replacement of bromine by the methoxy group was carried out in the usual manner by boiling the methyl alcoholic solution of the bromo compound under a reflux condenser with an excess of freshly prepared silver carbonate. The heptacetyl methyl maltoside was purified by recrystallization from 95% alcohol until its rotation became constant. The pure substance melted at  $125^{\circ}$  (uncorr.). A chloroform<sup>1</sup> solution containing 1.5781 g. in 50 cc. solution rotated  $6.75^{\circ}$  to the right in a 4 decimeter tube, hence  $[\alpha]_D^{20} = +53.5^{\circ}$ . A duplicate measurement, using 3.0005 grams in 50 cc., gave  $[\alpha]_D^{20} = 53.8^{\circ}$ .

**Purification of Heptacetyl Methyl Celloside.**—Part of the acetobromocellose employed was made from cellose by the action of acetic anhydride saturated with hydrobromic acid; the remainder was prepared by dissolving the octacetate of cellose in glacial acetic acid saturated with hydrobromic acid, in accordance with the directions given by Fischer and Zemplén.<sup>2</sup> The bromo compound is easily obtained crystalline and in good yield by either method. The preparation and purification of the acetylated methyl celloside was carried out in precisely the same way as that followed in making the heptacetyl methyl maltoside. The pure substance melted at  $187^{\circ}$  (uncorr.). A chloroform<sup>1</sup> solution containing 1.4962 grams in 50 cc. solution rotated  $3.00^{\circ}$  to the left in a 4 decimeter tube, hence  $[\alpha]_D^{20} = -25.1^{\circ}$ . A second measurement, using 3.0588 g. in 50 cc., gave  $[\alpha]_D^{20} = -25.7^{\circ}$ .

**Purification of Maltose Heptacetate.**—The sirupy acetyl bromomaltose was dissolved in acetone and shaken for several hours with freshly prepared silver carbonate. As soon as the bromine had been completely replaced, the silver salts were filtered off, and the acetone solution was evaporated under low pressure until crystallization occurred spontaneously. The mother liquor from this crystallization yielded a further quantity of crystals on the addition of ether. The material was recrystallized by adding ether to its chloroform solution. The specific rotation was lowered by sixteen recrystallizations from  $+78^{\circ}$  to the constant value  $[\alpha]_D^{20} = +67.8^{\circ}$  in chloroform.<sup>2</sup> The pure substance melted at  $181^{\circ}$  (uncorr.). Mutarotation occurs in chloroform, the rotation rising in about five weeks to the value  $+110^{\circ}$ ; a drop of dilute ammonia added to the solution brings the mixture to the same equilibrium in a few hours. The initial rotation of the pure substance in acetylene tetrachloride was found to be  $+65.0^{\circ}$ , rising slowly to  $+95.4^{\circ}$ . As acetyl determinations

<sup>1</sup> Chloroformum Purificatum, U. S. P.

<sup>2</sup> *Ber.*, 43, 2537 (1910).

do not appear to have been made on any of the heptacetates of the disaccharides, we hydrolyzed two half-gram portions of the pure compound with  $N/4$   $H_2SO_4$  and found 46.82 and 47.23%  $CH_3CO$  in comparison with 47.36%, the theoretical value.

**Purification of Cellose Heptacetate.**—The method used for preparing cellose heptacetate was in every way similar to that for the corresponding maltose derivative, except that the former did not crystallize spontaneously from acetone solution. Crystallization took place almost immediately, however, on adding ether after distilling off most of the acetone. The substance was recrystallized eighteen times by adding ether to its solution in chloroform, whereby the melting point was raised from  $195^\circ$  to  $204^\circ$  (uncorr.), and the specific rotation in chloroform<sup>1</sup> was lowered from  $+18^\circ$  to  $-2.4^\circ$ , without, however, reaching a constant value. The compound mutarotates in chloroform, the rotation of the equilibrium mixture being  $+22.6^\circ$ . Two half-gram portions of the substance rotating  $+5^\circ$  showed, on analysis, 47.56 and 47.67%  $CH_3CO$ ; theoretical, 47.36%.

**Preparation of Lactose Heptacetate.**—Acetobromolactose was prepared in crystalline form by treating lactose with a saturated solution of hydrobromic acid in acetic anhydride. The acetone solution of the bromo compound was shaken with freshly prepared silver carbonate until a few drops filtered from the mixture and diluted with water gave no precipitate with silver nitrate solution. The silver salts were then filtered off and the filtrate evaporated to a thick sirup under diminished pressure. At first considerable difficulty was encountered in crystallizing the heptacetate, but we have found that if the acetone solution is evaporated to a sufficiently high concentration, the addition of several times its volume of ether invariably causes crystallization in a few minutes. The yield of crude product is about 60-70% of the weight of sugar taken. The substance can be recrystallized without difficulty by adding ether to its chloroform solution, and if the amount of ether added is relatively small, the compound comes out very slowly in beautiful transparent prisms, often half a centimeter in length. Twenty such recrystallizations lowered the specific rotation in chloroform<sup>1</sup> from  $+12$  to  $-0.3^\circ$ , although even then a constant value was not reached. The purest material obtained melted at  $83^\circ$  (corr.). In its general properties, lactose heptacetate closely resembles the corresponding compounds of maltose and cellose, although it is considerably more soluble than either in alcohol, acetone and chloroform. Like them, it mutarotates in solution, the rotation in chloroform rising to  $+52.8^\circ$ .

The substance was identified as a lactose derivative by saponification with alcoholic potash, the resulting sugar being recognized as lactose by its rotatory power in water.

<sup>1</sup> Chloroformum Purificatum, U. S. P.



On combustion 0.1628 and 0.2025 g. subs. yielded 0.2913 and 0.3659 g.  $\text{CO}_2$  and 0.0863 and 0.1059 g.  $\text{H}_2\text{O}$ , corresponding to 48.8 and 49.2% C and 5.93 and 5.85% H. Calc. for lactose heptacetate ( $\text{C}_{28}\text{H}_{34}\text{O}_{18}$ ): 49.3% C and 5.70% H.

An acetyl estimation was made by boiling two half-gram portions for four hours with 100 cc.  $N/4$   $\text{H}_2\text{SO}_4$  in a quartz flask with a quartz reflux condenser, yielding 47.05 and 47.45%  $\text{CH}_3\text{CO}$  in comparison with the theoretical value, 47.36%.

WASHINGTON, D. C.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE ILLINOIS WESLEYAN UNIVERSITY.]

## THE QUANTITATIVE DETERMINATION OF MORPHINE IN THE VARIOUS ORGANS WHEN INJECTED INTO CATS AND RABBITS.

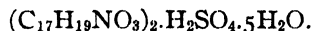
By A. W. HOMBERGER AND J. C. MUNCH.

Received May 6, 1916.

During the past few years one of the authors has had submitted to him, at different times, organs from cadavers for the analysis of poisons—especially morphine and opium. In two cases, the suspects had been embalmed. In one case after seven days, and in the other after fifteen days, of interment, the liver, kidneys, stomach and spleen were brought for examination. The quantitative relations as well as the general chemical conduct of the alkaloids found in the different organs, raised the question as to whether this was due to the embalming fluid, or whether the length of time after burial were the cause of the fluctuating assimilation and distribution.

The following paper deals with a series of experiments carried out on cats and rabbits in order to find, if possible, what the effect of the embalming would be on the amount of alkaloid in the different organs in case death had resulted from alkaloid poisoning, to ascertain how much of the original product could be recovered under those conditions, and to find what organs might be the strongest assimilators of such alkaloids. The alkaloid used in this case was morphine.

The morphine used in these investigations was Merck & Company's "Morphinae Sulphas," U. S. P. VIII. Qualitative examination showed it to be free from foreign materials such as starch or other opium alkaloids. Quantitative determinations of the morphine present, by Mayer's Reagent, and determinations of the sulfuric acid present, as barium sulfate, showed that the morphine sulfate used agreed with the formula



The desired amount of morphine sulfate was weighed out on an analytical balance, dissolved in distilled water and hypodermically injected into the mesenteric circulation. After a lapse of three hours, to allow for fixation in the organs of the body, the animals were chloroformed

and embalmed by cavity and arterial injection of a formaldehyde embalming fluid.

When the bodies were opened for analysis, the organs were always removed in the same order, first the stomach and intestines together, then, in order the spleen, liver, lungs, heart, kidneys, bladder and urine, and finally the brain. Then any parts wanted for qualitative analysis were cut out. Analyses were commenced at once to avoid any changes due to further decomposition.

Autenrieth's<sup>1</sup> modification of the Stas-Otto process was used, with several variations, for all the quantitative extraction of the organs. A longer time of extraction (five hours),<sup>2</sup> three extractions with ether in both acid and sodium hydroxide solution, and Pückner's technic of final extraction by hot amyl alcohol in slightly ammoniacal solution were used. The extracted morphine was dried at 60°, and calculated to its equivalent weight of morphine sulfate. Titrations of this residue agreed, within the limits of experimental error, with the gravimetric results obtained above. Qualitative tests of all residues were made to prove that the extractions were complete.

Dragendorff's<sup>3</sup> method was used for the analyses of both blood and urine. Puckner's<sup>4</sup> precautions were again followed. The extracted morphine was calculated to morphine sulfate, as in the Autenrieth extraction above. The weights in the following table are all expressed as morphine sulfate,  $(C_{17}H_{19}NO_3)_2 \cdot H_2SO_4 \cdot 5H_2O$ .

As may be noted in the table, the urine contains the largest single amount found in cats. The organs may be ranked according to morphine content, as the liver, kidneys, spleen and stomach. The urine content shows a great fluctuation, which is explained by Magnus<sup>5</sup> by the great variation in urinary secretion in animals, due to various factors such as quantity of food and water consumed, fecal excretion and animal idiosyncrasy. The appearance of morphine in the stomach of a cat following hypodermic mesenteric injection, is a matter of interest. Although only a small quantity is present, its constant appearance is similar to the case of arsenic, which, irrespective of the mode of introduction, always appears in the stomach. The constancy of results in the spleen extraction is important, the spleen of all organs, in both cats and rabbits, being subject to least variation in morphine content.

The results of extraction from rabbits are subject to less fluctuation during the course of the experiments, than with cats during the corresponding period. Arranged in order of morphine content, the results rank

<sup>1</sup> Autenrieth, "Detection of Poisons," 1915, p. 57.

<sup>2</sup> THIS JOURNAL, 23, 420 (1901).

<sup>3</sup> A. W. Blyth, "Poisons," 1906, p. 313.

<sup>4</sup> THIS JOURNAL, 23, 420 (1901).

<sup>5</sup> Münch. Med. Woch., No. 28 (1906).

as kidneys, liver, urine, spleen and stomach. Rabbit "E" differed from the others, in that it received a larger dose of morphine, and was not embalmed. That the urine contains the greatest quantity of morphine agrees entirely with the results of Van Kaufmann-asser,<sup>1</sup> of Van Ryn,<sup>2</sup> and of Dorlencourt,<sup>3</sup> drawn from the analyses of rabbits killed with morphine.

TABLE I.

Data obtained from experimental results.

Morphine in the organs of cats, as gram morphine sulfate.

	Cat A. G.	Cat B. G.	Cat C. G.
Kidneys.....	0.040	0.032	0.027
Liver.....	0.055	0.057	0.042
Spleen.....	0.031	0.023	0.020
Stomach.....	0.005	0.002	0.005
Urine.....	0.064	0.031	0.043
Total found.....	0.195	0.145	0.137
Total injected.....	0.200	0.200	0.200
Percentage found.....	97.5%	72.5%	68.5%
Length of burial.....	Analysis started im- mediately after death		
		One month	Three months

• TABLE II.

Morphine in the organs of rabbits, as gram morphine sulfate.

	Rabbit A. G.	Rabbit B. G.	Rabbit C. G.	Rabbit D. G.	Rabbit E. G.
Kidneys.....	0.0757	0.0654	0.0621	0.0473	0.0111
Liver.....	0.0601	0.0580	0.0574	0.0437	0.0214
Spleen.....	0.0122	0.0121	0.0120	0.0101	0.0343
Stomach.....	0.0060	0.0057	0.0052	0.0045	0.0072
Urine.....	0.0340	0.0304	0.0314	0.0311	0.0421
Total found.....	0.1889	0.1716	0.1681	0.1367	0.1161
Total injected.....	0.2000	0.2000	0.2000	0.2000	0.5000
Percentage found...	94.5%	89.8%	84%	68.4%	23%
Length of burial....	Analysis started immediately after death				
		2 weeks	4 weeks	6 weeks	8 weeks
					Unembalmed

Qualitative analyses of the tissues surrounding the organs examined giving uniformly negative results, osmosis can not account for the gradual decrease in morphine content. From the preceding results, it would seem that upon introducing morphine into the organs used in these anal-

<sup>1</sup> *Biochemische Ztg.*, 54, 161.

<sup>2</sup> Van Ryn, *Chemisches Zentralblatt*, 1908, [2] 174; *Pharmaceutisches Weekblad*, 44, 1353 (1907).

<sup>3</sup> *Compt. rend.*, 56, 1338.

yses, part of it combines with some cell constituent, forming a compound which is relatively more resistant to decomposition than is the uncombined morphine. Decomposition of the organ produces chemical compounds which break up the "free" morphine, but do not appreciably affect the "combined" morphine. This decomposition and removal of morphine produces the "preliminary drop" in morphine content observed.

The fairly constant results obtained between the close of this period and the beginning of the "secondary drop" represent the results of analyses made after the "free" morphine had been disintegrated, but before conditions were such that the "combined" morphine would be affected. This period of time is fairly constant for all the animals studied.

The gradual disintegration of the "combined" morphine, starting when conditions became favorable, would account for the "secondary" drop in morphine content. This decomposition would probably lead to complete removal from the body of all morphine as such.

This conclusion is best shown by the kidneys and liver, while the constant results for the spleen would seem to indicate that all the morphine deposited in that organ was present during decomposition as "combined" morphine, which began decomposition at the same time as the "combined" morphine of the other organs.

### Summary.

From the preceding work the following conclusions may be drawn:

(1) By means of a five-hour extraction, and three extractions with ether in both acid and sodium hydroxide solution, Autenrieth's modification of the Stas-Otto process is capable of yielding 97.5% of the morphine injected into an animal, if analysis be started very soon after death.

(2) The presence of formaldehyde as embalming fluid, has no appreciable effect upon the extraction results.

(3) The loss of morphine from a cadaver proceeds in two stages, a preliminary drop due to the splitting up of the "free" morphine present, then a period during which the morphine content is fairly constant, followed by a secondary drop, due to the splitting up of the "combined" morphine, *i. e.*, that morphine which had combined with some cell constituent, thus escaping the preliminary decomposition.

(4) The "secondary" decomposition is greatly retarded by embalming, although there seems to be no effect on preliminary disappearance.

(5) Results of analyses of cats and rabbits which have received hypodermic injections of morphine, embalmed and subsequently analyzed, may be interpreted successfully by this theory of "combined morphine."

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY,  
No. 273.]

## ON THE PRODUCTS OF THE ACTION OF CERTAIN AMYLASES UPON SOLUBLE STARCH, WITH SPECIAL REFER- ENCE TO THE FORMATION OF GLUCOSE.

By H. C. SHERMAN AND P. W. PUNNETT.

Received June 22, 1916.

Probably the first recognized case of what we now know as enzyme action was the observation by Kirchhoff (1814), confirmed and amplified by Dubrunfaut (1823) and by Payen and Persoz (1833), that a substance contained in barley malt is active in hydrolyzing starch with the production of reducing sugar. The sugar thus formed was for some time assumed to be glucose but later was shown by O'Sullivan<sup>1</sup> to be, at least chiefly, maltose. During the forty years since the publication of O'Sullivan's work several investigators have studied the kinds and amounts of products formed by the action of this and other amylases, but with widely varying results. The evidence as to the formation of glucose as a digestion-product of malt extract or pancreatic juice, for example, is conflicting<sup>2</sup> and among those who accept the affirmative evidence there is no apparent consensus of opinion as to whether the formation of glucose is due to the action of amylase or of a maltase simultaneously present. The general tendency to regard enzyme action as very highly specific has naturally favored the latter assumption and there has been no adequate evidence of the formation of glucose directly by amylase because in the work previously published on this subject the amylolytic agents used have been natural secretions, extracts, or simple alcohol precipitates which might have contained other enzymes along with the amylase. A reinvestigation of the question of the formation of glucose by the action of amylase was therefore undertaken.

### Methods and Results.

The general plan of the present work was to allow pancreatic and malt amylases and the amylase of *Aspergillus oryzae*—chosen as representative

<sup>1</sup> *J. Chem. Soc.*, 25, 579 (1872); 29, 478 (1876); 30, 125 (1876).

<sup>2</sup> V. Mering and Musculus, *Z. physiol. Chem.*, 1, 395 (1878); 2, 403 (1878); Brown and Heron, *J. Chem. Soc.*, 35, 596 (1879); Atkinson, *Chem. News*, 41, 169 (1880); V. Mering, *Z. physiol. Chem.*, 5, 185 (1881); Brown and Morris, *J. Chem. Soc.*, 47, 527 (1885); Kellner, Mori and Nagaoka, *Z. physiol. Chem.*, 14, 296 (1889); Lea, *J. Physiol.*, 11, 226 (1890); Külz and Vogel, *Z. Biol.*, 31, 108 (1894); Brown and Morris, *J. Chem. Soc.*, 67, 309, 709 (1895); Ling and Baker, *Ibid.*, 67, 702, 739; 71, 508; Krober, *Z. ges. Brauw.*, 18, 325, 334 (1895); *Chem. Zentrbl.*, 66, 1021; Chlodounsky and Sulc, *Jahr. Thierchem.*, 26, 27 (1896); Brown, Morris and Millar, *J. Chem. Soc.*, 71, 72, 109, 115 (1897); Brown and Millar, *Ibid.*, 75, 315 (1899); Baker, *Ibid.*, 81, 1177 (1902); Ling and Davis, *Ibid.*, 82, 732 (1902); Clemm, *Pflüger's Archiv. f. d. ges. physiol.*, 89, 517 (1902); Davis and Ling, *J. Chem. Soc.*, 85, 16 (1904); Bierry, *Compt. rend.*, 141, 146 (1905); 143, 300 (1906); 146, 417 (1907); Kita, *J. Ind. Eng. Chem.*, 5, 222 (1913).

of the starch-splitting enzymes of the higher animals, higher plants, and fungi, respectively—to act upon soluble starch under comparable and carefully controlled conditions, and then to examine the digestion products for glucose both by means of the osazone reaction and by quantitative measurements of reducing and rotatory powers.

The enzymes have been used both in their commercial forms and after laboratory purification and, in general, have been allowed to act in the presence of such amounts of salt and phosphate as had been found in previous tests in this laboratory to be favorable to the action of each of these amylases. The ratios of enzyme to substrate usually approximated those with which we have to deal in determinations of diastatic power or in such studies of these enzyme hydrolyses as have been described in previous papers.<sup>1</sup> In all cases the temperature at which the enzyme was allowed to act was 40°.

The experiments here described were carried out in two series—the first in 1912, the second in 1914–15.

**Series of 1912.**—In the experiments of this first series, carried out with the coöperation of Mr. David F. Renshaw, attention was chiefly devoted to the evidence to be obtained by application of the osazone reaction. The previous work in this laboratory regarding the influence of concentration of glucose and presence of maltose<sup>2</sup> was supplemented by the following observations: Using 0.4 g. of freshly purified phenylhydrazine hydrochloride with 0.6 g. of sodium acetate in a volume of 4 cc. it was found possible to obtain recognizable osazone from 10 mg. of glucose, after one hour's heating in the boiling water bath; but in the presence of several times its weight of maltose the glucose reacted much less readily.

When the amount of sodium acetate was increased to 0.8 g. (for 4 cc. of the test solution) the test appeared to be improved; this amount was therefore used in all subsequent experiments.

On applying the test to mixtures of glucose and maltose totaling 0.20 g. (the "standard" weight of sugar for the application of the osazone test in a volume of 4 cc.) the following results were obtained:

Percentage composition of sugar mixture, Glucose.....	10	9	8	7	6	5	4
Maltose.....	90	91	92	93	94	95	96
Minutes of heating for appearance of glucosazone.....	17	22	26	30	33	51	60

These results indicate the possibility of detecting by this application of the osazone test as little as 4% of glucose in a mixture of glucose and maltose alone, and of roughly judging the amount of glucose when present in somewhat larger proportion in such a mixture.

Dextrin was found to cause a marked retardation, even when present

<sup>1</sup> THIS JOURNAL, 32, 1073, 1087; 33, 1195; 34, 1104; 35, 1617, 1784, 1790; 37, 623, 643, 1305.

<sup>2</sup> Sherman and Williams, *Ibid.*, 28, 629 (1906).

to the extent of only 10% of the total carbohydrate, and if in excess of that proportion, it rendered the formation of the glucosazone very uncertain. Since it was to be expected that the mixtures of digestion products obtained by amylase action at 40° would contain at least 10% of dextrin, and probably 20% even when the action was long continued, it appeared impossible to use the digestion mixtures directly for the osazone tests. Two methods for removing the dextrin were suggested by work of previous investigators—to precipitate the dextrin by pouring the solution into alcohol; or to evaporate the solution to dryness and extract with alcohol. The precipitation method did not give good results when tried on known mixtures of glucose, maltose and dextrin—possibly because of adsorption of glucose by the precipitated dextrin or because of partial solubility of the dextrans in the alcohol solution. The second method proved better; practically no dextrin was extracted by the alcohol, and the relative solubility of glucose in hot 95% alcohol (about five times that of maltose according to Lippman), made possible the extraction of most of the glucose by the use of small amounts of the solvent. The procedure, as finally worked out, was as follows:

The digestion mixture, which had been kept at 40° for the required time, was heated to boiling to stop the enzyme action and (usually after the determination of the rotatory and reducing powers) was evaporated to dryness on a water bath with the addition of some clean sand to render the mass more porous and facilitate its subsequent extraction. The dry mass of carbohydrates, salts and sand was then boiled for two minutes, with constant and vigorous stirring with 20 cc. of 95% ethyl alcohol. The alcohol extract was decanted off while hot and evaporated to dryness on the water bath. The sugar thus extracted was weighed and dissolved in twenty times its weight of water and 4 cc. of this solution used for each osazone test. If the digestion has been long continued, about 10–15% of the mass is extracted in this way. If the starch conversion is very incomplete, it is generally necessary to repeat the extraction process in order to obtain a sufficient quantity of reducing sugar for satisfactory testing.

This method was applied to the digestion products resulting from the action of the following amylase preparations: (1) a high grade commercial pancreatin powder furnished by Parke, Davis and Company; (2) a highly purified and very active preparation of pancreatic amylase made in this laboratory; (3) malt amylase preparations purified in the laboratory but not representing as high a degree of activity as was reached later; (4) a preparation, kindly furnished us by Dr. J. Takamine, which contained the amylase of *Aspergillus oryzae* and showed about four times the diastatic power of ordinary commercial takadiastase. In all of these cases the sugar extracted from the digestion mixture gave an osazone reaction for glucose when tested as above described. In nearly all cases, however, the reaction was very slight. Only in the extract from the products of long-continued (18 hours) action of taka diastase (containing the amylase of *Aspergillus oryzae*) was there indication of one-tenth as much glucose as maltose.

Several different samples of commercial pancreatin were allowed to act upon soluble starch for 39 hours at  $40^{\circ}$  and the digestion products then tested as above described. In all of these cases the osazone reaction gave evidence of glucose.

**Series of 1914-5.**—In this second series of experiments the enzymes were used in such concentrations as to be as nearly as practicable equivalent in amylolytic power, the quantity of enzyme preparation employed in each case being such as would digest the starch present to disappearance of blue or violet color-reaction in 30 minutes. Activating salts were used as in the first series, and the general arrangement of the experiments was the same as before, the digestion products being evaporated on sand and extracted with alcohol. Special attention was devoted to the purification of the water and salts used. Digestions were conducted at  $40^{\circ}$  and usually for 24 hours—48 times as long as was required for the digestion of the starch to products giving no blue or violet color with iodine. The reducing and rotatory powers of the organic solids of the digestion mixture and of its alcohol extract were determined, and compared with those of pure maltose. A higher reducing power or lower rotatory power than would be shown by an equal weight of pure maltose was taken as evidence of the presence of glucose in the solids extracted by the 95% alcohol from the evaporated digestion mixture (for if any dextrin had been extracted the effect would have been to alter each of these properties in the opposite direction).

The procedure for each experiment was as follows: A quantity of soluble starch, usually equivalent to 8 g. of dry matter, was dissolved in pure boiling water and, after the addition of the measured amount of the salts necessary to give the proper concentration of activator in the final solution, the solution made up to such a volume as, after the subsequent addition of the required amount of enzyme solution, would give a starch concentration of 2% in the digestion mixture. The flask was then immersed in the constant temperature bath until it had reached  $40^{\circ}$ , after which the enzyme solution was added, the flask stoppered with a plug of cotton and left in the bath for 24 hours.

At the expiration of this time it was removed, boiled to stop the enzyme action and filtered to remove the small amount of suspended matter. Considerable difficulty was experienced in this filtration. The best method was found to be by the use of Gooch crucibles containing thin pads of washed asbestos. By using three such crucibles in rotation it was possible to filter 400 cc. of solution in a few hours. This insoluble suspended matter always amounted to about 1% of the weight of the starch.

The filtered solution was often greater than the required volume and the subsequent evaporation usually produced a gelatinous precipitate, of a few milligrams weight, which was also filtered out.

The filtered solution was then made up to volume and an aliquot portion (one-tenth) was withdrawn for use in the determination of rotatory and reducing powers. Another such portion was evaporated to dryness on a water bath in a weighed glass evaporating dish containing some ignited, clean sand and then dried to constant weight by heating at  $70^{\circ}$  under a reduced pressure of 40 to 100 mm. This weight of



material corrected for the weight of enzyme and of dry activator gave the total soluble carbohydrates.

The remaining four-fifths of the solution was also evaporated on the water bath, with the addition of sand. This mixture of carbohydrate, activating salt and sand was next extracted on the water bath with boiling 95% alcohol in 20 cc. portions. The alcohol extract was evaporated to dryness, dissolved in water, and made up to a volume of 100 cc. with filtration if necessary. Ten cc. of this solution were withdrawn and used for the determination of solids as in the case of the original solution. The rotatory and reducing powers were determined as described above.

The residue left with the sand after the alcohol extraction was dissolved in hot water, filtered, and made up to 250 cc. Fifty cc. (or sometimes 25 cc.) were used for the total-solids determination and the rotatory and reducing power determined on a portion and calculated to the basis of dry carbohydrate material.

Finally the remainder of the extract solution was evaporated until each cubic centimeter contained 0.1 g. of carbohydrate and 2 cc. of this solution used in each osazone test—using 0.3 cc. of pure phenylhydrazine, 0.2 cc. of 87% acetic acid (equivalent to the phenylhydrazine base), 0.3 g. of sodium acetate, 2.0 cc. of sugar solution and 1.5 cc. of water, giving a total volume of 4 cc.

### Summary of Results.

**Pancreatic amylase** tested both in the form of commercial pancreatin and as a highly active purified preparation made by Miss M. D. Schlesinger from this same pancreatin as previously described<sup>1</sup> resulted in an extract having greater reducing power than pure maltose which, as explained above, is taken as evidence of the presence of glucose. The osazone reaction for glucose was negative in all of these extracts, indicating that the yield of glucose was small as compared with the large amount of maltose produced. The close agreement of results obtained from the action of the commercial pancreatin and of the purified amylase made from it suggests that such glucose production as occurs is attributable to the action of the amylase rather than of a separate enzyme (maltase); for it is hardly reasonable to suppose that a maltase, present as a separate substance in the pancreatin, would have remained with the amylase in unchanged ratio throughout the purification process.

**Malt amylase** was tested in the form of a purified preparation<sup>2</sup> and parallel experiments were made with malt extract. The measurements of reducing and rotatory powers of the sugars extracted as above described indicated that, along with a large amount of maltose, a small proportion of glucose had been formed both by the malt extract and by the purified malt amylase. The osazone tests for glucose were negative in these cases, the amount of glucose in the digestion mixture being too small to be demonstrated by this test, even as applied to the solids obtained by alcohol extraction.

<sup>1</sup> Preparation 62 II made as described by Sherman and Schlesinger (*THIS JOURNAL*, 34, 1105 (1912)) and showing a diastatic power of 3313, equivalent to about 5000 on Lintner's scale.

<sup>2</sup> Preparation 111A. Sherman and Schlesinger, *THIS JOURNAL*, 37, 648 (1915).

It thus appears that both pancreatic and malt amylases, even when highly purified, are not limited to the formation of maltose but may form some glucose as well; but that under conditions such as obtained in the determination of diastatic power the proportion of glucose formed is so minute as to be practically negligible in comparison with the much greater amounts of maltose formed.

**Takadiastase** and the partially purified **amylase of *Aspergillus oryzae*** prepared from it by Dr. A. P. Tanberg,<sup>1</sup> when tested in a manner parallel to the experiments with pancreatic and malt amylases just described, produced a larger yield of glucose, but here also maltose was the chief digestion product even though the digestion was continued 40 to 50 times as long as was required for the disappearance of the starch-iodine reaction.

When commercial takadiastase, in quantity sufficient to digest all the starch present in one-half hour to disappearance of the starch-iodine reaction, was allowed to act for 24 hours (at 40° and in the presence of activating salts), the analysis of the resulting digestion mixture and its alcoholic extract indicated that of the total carbohydrate present more than half was maltose, about one-fourth was glucose, and somewhat less than one-fourth was dextrin.

The amylase preparation made from the takadiastase and representing a considerable degree of purification and concentration of both amyloclastic and saccharogenic power, formed in a parallel experiment a somewhat smaller proportion of glucose. This may be due either to the elimination of a maltase in the purification process or to the fact that the purified amylase is less stable than the commercial and therefore would not show as great relative activity in a long as in a short digestion experiment.

**With all three types of amylase** it is noticeable that considerable quantities of dextrin still appear among the digestion products, even when the digestion is allowed to proceed forty to fifty times as long as is required for the disappearance of the starch-iodine reaction.

On the other hand, many of our experiments have shown a larger yield of reducing sugar and smaller yield of dextrin than would correspond with the "resting stage" described by some of the earlier investigators.

The different enzymes all left about 1% of the weight of the "soluble" starch as a very finely divided difficultly filtrable insoluble residue.

There are indications that dextrin, maltose and glucose may not constitute the sole products of the action of amylases upon soluble starch.

### Conclusion.

The experiments lead to the conclusion (1) that any of the amylases

<sup>1</sup> The material here used was Dr. Tanberg's Preparation No. 15 having a diastatic power of 194 ("new scale") which is about 8 times the activity of commercial takadiastase but somewhat less than half the maximum activity thus far attained. See Sherman and Tanberg, *THIS JOURNAL*, 38, 1638.

	Experiments with Commercial Takadiastase.			Experiments with Malt extract.		
	No. 3.	No. 4.	No. 5.	No. 6.	No. 7.	No. 8.
1. Dry starch (g.).....	8.0	8.0	8.0	8.0	8.0	8.0
2. Insoluble (g.).....	0.1157	0.1103	0.0994	0.1140	0.1039	0.0904
3. Insoluble (%).....	1.44	1.38	1.24	1.43	1.30	1.13
4. Sol. carb. in T (g.).....	8.488	8.393	8.313	8.193	8.154	8.204
5. Total carb. in T (g.).....	8.6037	8.5033	8.4124	8.307	8.258	8.2944
6. Increase (g.).....	0.6037	0.503	0.4124	0.307	0.258	0.2944
7. Increase (%).....	7.55	6.28	5.15	3.84	3.22	3.68
8. $[\alpha]_D$ of T.....	126.49°	126.7°	129.1°	142.9°	141.95°	142.7°
9. "R" in maltose (g.).....	8.245	8.105	8.290	7.610	7.670	7.920
10. "R" in glucose (g.).....	5.040	4.950	5.060	4.645	4.680	4.830
11. Alc. used in extraction (cc.).....	200	300	300	200	150	<div> <div>Part I.</div> <div>200(abs.)</div> <div>100(5%)</div> </div>
12. Carb. in X (g.).....	2.907	3.864	4.310	3.382	3.666	0.566 1.633
13. Corresp. carb. in T (g.).....	3.6338	4.830	5.388	4.2275	4.583	0.707 2.041
14. $[\alpha]_D$ of X.....	102.12°	108.6°	107.02°	128.2°	132.5°	130.7° 130.1°
15. "R" in maltose (g.).....	3.272	4.490	4.901	3.360	3.717	0.568 1.685
16. "R" in glucose (g.).....	1.995	2.739	2.990	2.048	2.270	0.345 1.029
17. Carb. in R (g.).....	3.6594	2.701	2.153	3.306	2.844	2.712 1.640
18. Corresp. wt. in T (g.).....	4.574	3.376	2.691	4.132	3.555	3.390 2.05
19. $[\alpha]_D$ of R.....	152.8°	159.7°	183.7°	150.8°	153.8°	142.6° 151.2°
20. "R" of R in maltose (g.).....	3.256	2.154	1.692	2.686	2.470	2.582 1.480
21. "R" in glucose (g.).....	1.988	1.314	1.032	1.652	1.506	1.576 0.904
22. Corresp. X and R (g.).....	8.268	8.206	8.079	8.360	8.138	8.188
23. Sol. carb. in T + malt ext. solids.....	.....	.....	.....	8.345	8.315	8.364
Loss carb. (g.).....	0.280	0.187	0.234	(Gain 0.015)	0.177	0.176
Ozone tests in hot soln. (heated 2 hrs.)	.....	.....	.....	Negative	Negative	Negative

	Purified Malt Amylase. (Preparation 111A.)		Amylase of Aspergillus oryzae.		Commercial Pancreatin. (Pancreatin 6.)		Purified Pancreatic Amylase (62II).	
	No. 9.	No. 10.	No. 11.	No. 12.	No. 13.	No. 14.	No. 15.	No. 17.
Enzyme (mg.).....	4.6	7.7	3.3	3.75	1.71	6.0	0.2	0.6
Dry starch (g.).....	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0
Insoluble (g.).....	0.106	0.079	0.030	0.0864	0.0689	0.1014	0.0891	0.0966
Insoluble (%).....	1.35	0.99	0.38	1.08	0.86	1.27	1.11	1.21
Sol. carbohy. in T (g.).....	8.234	8.276	8.235	8.222	8.167	8.264	8.116	8.211
Total carbohydrate (g.).....	8.340	8.355	8.265	8.308	8.236	8.365	8.205	8.308
Increase (g.).....	0.340	0.355	0.265	0.308	0.236	0.365	0.205	0.308
Increase (%).....	4.25	4.44	3.31	3.85	2.95	4.56	2.56	3.85
[ $\alpha$ ] <sub>D</sub> of T.....	147.95°	146.9°	148.2°	144.8°	156.6°	132.9°	155.2°	157.5°
"R" in maltose (g.).....	7.210	7.140	7.220	7.465	6.340	6.515	6.030	5.955
"R" in glucose (g.).....	4.400	4.360	4.410	4.495	3.870	3.975	3.680	3.635
Alc. for extraction—95% (cc.).....	100	100	100	100	100	100	100	100
Carbohydrate in X (g.).....	2.119	1.884	2.542	1.850	1.845	1.602	1.206	1.303
Corresp. in T (g.).....	2.659	2.355	3.175	2.313	2.306	2.005	1.508	1.629
[ $\alpha$ ] <sub>D</sub> of X.....	130.3°	125.9°	136.4°	125.1°	138.2°	139.6°	137.0°	141.1°
"R" in maltose of X (g.).....	2.216	1.922	2.736	2.044	2.070	1.638	1.248	1.304
"R" in glucose of X (g.).....	1.352	1.172	1.668	1.246	1.262	1.000	0.762	0.794
Carbohydrate in R (g.).....	4.540	4.694	3.983	4.748	4.597	4.647	5.164	5.234
Corresp. in T (g.).....	5.674	5.868	4.978	5.935	5.746	5.809	6.455	6.543
[ $\alpha$ ] <sub>D</sub> of R.....	151.8°	154.0°	156.0°	151.2°	161.3°	164.9°	160.8°	162.75°
"R" in maltose of R (g.).....	3.390	3.793	3.073	3.953	3.058	3.568	3.748	3.465
"R" in glucose of R (g.).....	2.068	2.303	1.873	2.413	1.865	2.178	2.288	2.115
Corresp. X and R (g.).....	8.333	8.223	8.153	8.248	8.052	7.814	7.963	8.172
Loss carboh. in process (g.).....	0.99 (gain)	0.053	0.082	0.026 (gain)	0.184	0.450	0.153	0.039
Ozone tests.....	Negative	Negative	17 min.	12 min.	Negative	Negative	Negative	Negative
Barford tests.....	.....	.....	.....	Positive	White ppt. no red	Same as No. 13	Same as No. 13	Same as No. 13

here studied may form some glucose, (2) that in such conditions as obtain in the usual determinations of diastatic power the yield of maltose so far predominates as to justify the custom of calculating the reducing powers of the digestion products as if due to maltose alone.

#### Detailed Data of the Principal Experiments of the Series of 1914-5.

In the above tables, the data are recorded under abbreviated captions, the significance of which are as follows:

(1) is the weight of dry starch used. (2) is the weight of insoluble matter filtered out. (3) is the percentage of the dry starch consisting of such insoluble matter. (4) is the weight of soluble carbohydrates in the total solution; *i. e.*, total solids less activation salts, less enzyme. (5) is the sum of (2) and (4). (6) is the difference between (5) and (1). (7) is the percentage increase in weight over the weight of dry starch used. (8) is the specific rotatory power for the soluble carbohydrates in the total solution ("T"). (9) is the reducing power expressed in terms of maltose, and (10) in terms of glucose for the whole solution. (11) is the amount of alcohol used for the extraction. (12) is the weight of carbohydrates in the extract solution ("X") and (13) is the weight equivalent to the total solution; *i. e.*,  $(12) \times 1.25$ , since the extraction was made on four-fifths of the original material. (14) is the specific rotatory power for the carbohydrates in the extract solution. (15) and (16) are the reducing power of the extract solution expressed in terms of maltose and glucose, respectively. (17) is the weight of carbohydrate in the residue solution ("R"), *i. e.*, total solids less four-fifths the weight of added activator. (18) is the portion of soluble carbohydrates in the original total solution corresponding to the weight in the residue solution. (19) is the specific rotatory power of the carbohydrates in the residue solution and (20) and (21) their reducing power expressed in terms of maltose and glucose, respectively. (22) is the sum of (13) and (18) and when subtracted from (4) gives the loss of material (23) due to the process.

LABORATORY OF FOOD CHEMISTRY.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY,  
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### EXPERIMENTS UPON STARCH AS SUBSTRATE FOR ENZYME ACTION.

By H. C. SHERMAN AND J. C. BAKER.

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The forms in which starch has been used as substrate for enzyme action may be grouped as: (1) Natural starch dispersed in water under different conditions of time, temperature, and pressure but without "chemical" treatment; (2) starch which has been subjected to the action of acid (Lintner)<sup>1</sup> or to other chemical treatment (Wolff and Fernbach)<sup>2</sup> to render it "soluble;" (3) fractions of the starch substance which have been separated from the remainder by sedimentation (Tanret),<sup>3</sup> or pre-

<sup>1</sup> *J. prakt. Chem.*, [2] **34**, 378 (1886); see also Ford, *J. Soc. Chem. Ind.*, **23**, 414 (1904).

<sup>2</sup> *Compt. rend.*, **140**, 1403 (1905); **143**, 363, 380 (1906).

<sup>3</sup> *Bull. soc. chim.*, [4] **17**, 83 (1915).

cipitation (Maquenne and Roux,<sup>1</sup> Fernbach,<sup>2</sup> Malfitano and Moschkoff,<sup>3</sup> Gruzewska<sup>4</sup>).

In order to ensure uniformity of substrate in successive experiments and to avoid difficulties due to imperfect solution or unequal dispersion on the one hand, or on the other hand the use of substrate representing only a part of the original starch and perhaps contaminated by the reagent or solvent used in its preparation, the consensus of opinion of workers in this field has favored the use of "soluble" starch, prepared by Lintner's method of simply soaking the starch grains in cold hydrochloric acid and subsequently removing the latter by washing with cold water. Such "soluble" starch has been used in nearly all the studies of amylases carried on in this laboratory and has always been found a satisfactory substrate except for certain peculiarities encountered in the case of purified malt amylase.

When soluble starch is acted upon by pancreatic amylase either in purified or commercial form under the conditions used for measuring the amyolytic activities of enzyme preparations, the weight of maltose produced is regularly about half of the weight of starch which disappears. In other words the purified pancreatic amylase having many times the power of commercial preparations shows nevertheless the same relation between amyoclastic and saccharogenic powers.<sup>5</sup> Similarly in experiments upon the amylase of *Aspergillus oryzae*, the amyoclastic and saccharogenic activities were found to increase in about the same proportion as the enzyme was concentrated by purification.<sup>6</sup> But when purified malt amylase preparations were compared with malt extracts no such constancy in the ratio of amyoclastic and saccharogenic powers was found. In this case not only had the purification process altered the ratio of amyoclastic and saccharogenic activities, but evidently also the generally accepted method for measuring amyoclastic action (that of Wohlgemuth) yields misleading results when applied to purified malt amylase.

The present investigation had its origin in an attempt to prepare a substrate sufficiently homogeneous to yield reliable results when used as in the Wohlgemuth method, and developed from this into a study of the differing behavior toward enzymes of the two chief constituents of starch. It was thought that the discrepancy noted in the measurements of amyoclastic action of malt amylase might be due to an unequal susceptibility of the two main constituents of starch<sup>7</sup> to the action of the enzyme, in which

<sup>1</sup> *Compt. rend.*, 140, 1303 (1905); *Ann. chim. phys.*, [8] 9, 179 (1906).

<sup>2</sup> *Proc. 8th Intern. Congr. Appl. Chem.*, 13, 131 (1912).

<sup>3</sup> *Compt. rend.*, 150, 710 (1910); 151, 817 (1910).

<sup>4</sup> *Ibid.*, 146, 540 (1908); 152, 785 (1911).

<sup>5</sup> Sherman and Schlesinger, *THIS JOURNAL*, 35, 1784 (1913).

<sup>6</sup> Sherman and Tanberg, *Ibid.*, 38, 1638 (1916).

<sup>7</sup> Meyer (Untersuchungen über die Stärkekörner) considered starch to be chiefly

case an approximate separation of the substances might yield a more satisfactory substrate. At the same time it seemed very desirable that the material to be used as substrate in our experiments should not be subjected to treatment with strong reagents nor to solution and reprecipitation, which might involve danger of change in its behavior toward enzymes.

Experiments were, therefore, made to test the feasibility of extracting the more soluble component ("β-amylose," "amylose") while leaving behind the less soluble ("α-amylose," "amylopectin") by carefully regulated treatment of purified potato starch with distilled water. By ultrafiltration or by simple sedimentation we did not obtain satisfactory separations but by use of the centrifuge much better results were obtained.

### **Separation of "Soluble" and "Insoluble" Components of Starch by means of Centrifugal Force.**

When thin starch paste is submitted to centrifugal force it is separated into a lighter, clearer and more limpid layer containing the more soluble constituent (β-amylose of Meyer, amylose of Maquenne and Roux) and a heavier, opalescent, very viscous layer containing the less soluble component (α-amylose of Meyer, amylopectin of Maquenne and Roux, amylophosphate of Tanret). For the purpose of making such separations we have employed three different types of centrifuge, but in all of the experiments here described the Size 1, Type A, 8-tube centrifuge of the International Instrument Company has been used. In these experiments 50 cc. of the starch paste are placed in each of the 8 tubes of the centrifuge and rotated for 30 min. at about 2400 revolutions per min. ("relative force 1024 times gravity"). At the end of such treatment the liquid in each tube is found to have separated into two distinct layers, the heavier opalescent layer usually occupying from one-third to four-fifths of the total volume.

It was thus found possible to carry out a series of experiments, heating the starch with water under different conditions, separating the two portions composed of two substances to which he gave the names α-amylose and β-amylose. Maquenne and Roux (*Loc. cit.*) call about four-fifths of the starch substance "amylose" and about one-fifth "amylopectin." Gruzewska (*Compt. rend.*, 146, 540; 152, 785) by solution in alkali and precipitation with alcohol estimated the "amylopectin" to be 40 to 45% of the starch. Samec (*Koll. Beihefte*, 6, 32) by a modification of Gruzewska's method found 56% of "amylopectin" and only 44% of "amylose," the latter being practically phosphorus-free while the former contained phosphorus as an essential constituent. Tanret (*Bull. soc. chim.*, [4] 17, 83) by successive treatment of starches with hot water, sedimentation and decantation, finds from 70 to 80% of "amylopectin" or "amylophosphate" and 20 to 30% of "amylose." For the material present in larger quantity the term α-amylose not only has priority but is much more appropriate than the term amylopectin. We have, therefore, given preference to Meyer's terminology in this paper, even though some of Meyer's views as to the chemical nature and relationships of the α- and β-amyloses may not be tenable.

tions, observing their properties, and using them as substrates for the study of diastatic hydrolysis.

**Experiments upon Commercial Potato Starch.**—In the earlier of our experiments a good grade of commercial potato starch was used. The starch was handled in air-dry condition and allowance was made for the moisture which it contained when weighing out portions for experiment. All statements of weight or concentration of starch refer, therefore, to the water-free substance. Only one of these earlier experiments will be described here.

In this case starch was gelatinized in 100 times its weight of water at 85°, and the temperature maintained by means of a thermostat while the liquid was stirred continuously. Portions of the liquid were withdrawn and centrifuged at intervals. The centrifugates were studied with reference to volume, viscosity, concentration, and behavior under the action of pancreatic and malt amylases. In the enzyme experiments the time required for the digestion of starch to disappearance of blue iodine reaction, and to disappearance of red reaction with iodine, was observed, and the maltose which had been formed at the time of disappearance of blue iodine reaction was determined. The iodine tests were applied under the conditions prescribed by the Wohlgemuth method and the "disappearance of blue" was considered to be that point at which the color obtained with iodine changed from red-violet (RV) to violet-red (VR), the colors being always determined by comparison with the Milton-Bradley Standard Color Chart as given in Mullikin's *Identification of Pure Organic Compounds*. The data obtained are shown in Table I.

TABLE I.—PROPERTIES OF UNFILTERED CENTRIFUGATES FROM 1% POTATO STARCH PASTES PREPARED AT 85°.

Time of heating.....	1 hour	2 hours	4 hours	6 hours	8 hours
Volume of lower layer.....	60%	66%	65%	61%	47%
Volume of centrifugate.....	40%	34%	35%	39%	53%
Viscosity of centrifugate <sup>1</sup> .....	1.445	1.572	2.130	2.335	3.06
Concentration of starch in centrifugate.....	0.384%	0.444%	0.572%	0.716%	0.816%
Digestion with pancreatin:					
To disapp. of blue react. (Mins.)	10.0	11.5	14.5	18.5	20.0
To disapp. of red react. (Mins.)	20.0	24.0	32.0	42.0	46.0
Maltose at end of blue in percentage of starch..... (60.5)	48.5	46.2	48.8	44.7	
Digestion with malt amylase:					
To disapp. of blue react. (Mins.)	18.0	19.0	20.0	24.0	26.0
To disapp. of red react. (Mins.)	24.0	28.0	40.0	55.0	65.0
Maltose at end of blue in percentage of starch.....	83.2	81.2	75.0	69.2	68.0

<sup>1</sup> Viscosities are here expressed as time of flow of solution divided by time of flow of water, both at 30°, Ostwald viscosimeters being used.



When starch pastes are separated by centrifugal force as above described, the lower (heavier) layer is found to consist largely of greatly swollen grains. The swelling of the grains increases with duration of heating in water and appears to be due to absorption of water by the "insoluble" constituent of the starch grain, the "soluble" constituent going into solution.

From the data given in Table I for volumes of lower layers and centrifugates from pastes prepared by heating for five different lengths of time at each of three temperatures, it would appear that in this particular series of experiments the swelling of the grains and liberation of the soluble component was the chief effect of heating the starch in 100 times its weight of water up to about 2 hours at 85°, and that the chief result of further heating at 85° was dispersion (or hydration) of the insoluble component into forms (or derivatives) not removable from the centrifugate by the force here employed (about 1000 times gravity for 30 minutes). Microscopic examination showed that the upper layer did contain some swollen grains. In subsequent experiments these were removed by filtering through paper covered with a thin layer of absorbent cotton. Observations upon the iodine reactions and phosphorus content of the two layers obtained in this and several subsequent experiments also bear upon this phase of the problem. The results of the action of amylases upon the centrifugates obtained after different periods of heating in water at 85°, also throw light upon the nature of the starchy material contained in this layer, and upon the differing ratios of amylolytic to saccharogenic powers as between pancreatic and malt amylases. Thus it will be seen from the data given in Table I that the pancreatic amylase acted in much the same way upon the different substrates. The time required for the digestion of the material to a point where iodine no longer gave a blue or violet reaction ("disappearance of blue") was approximately proportional to the amount of starch material present, the time required for "disappearance of red" was approximately twice that for "disappearance of blue" in all cases, and the maltose found at the time when the blue reaction had just disappeared was always about half the weight of the original substrate, as had been found by previous workers in this laboratory in experiments in which the enzyme acted upon soluble starch prepared by the Lintner process. On the other hand, it is apparent that the malt amylase acted differently upon the substrates obtained after different lengths of heating. The time required for disappearance of the red reaction with iodine increased more than did the concentration of the substrate in the successive portions; and the relative yield of maltose at the time of disappearance of the blue reaction is greatest for the substrate first obtained and decreases progressively for the substrates prepared by longer heating.

All of the results are consistent and together they indicate plainly that the continued heating results in dispersion of more and more of the less soluble component of the starch ( $\alpha$ -amylose, amylopectin) into the solution of the more soluble component ( $\beta$ -amylose, amylose).<sup>1</sup>

With pancreatic amylase the digestion of the two components proceeds proportionately, so that the ratio of apparent amylolytic and saccharogenic activity is not materially disturbed by the difference in nature of the substrate; but with malt the two components are hydrolyzed quite differently, so that with increasing proportion of the less soluble component ( $\alpha$ -amylose, amylopectin) in the substrate the ratio of times required for disappearance of the blue and red reactions and the ratio of amylolytic and saccharogenic action are both altered.

**Experiments upon Potato Starch Prepared in the Laboratory.**—For the main series of experiments, starch was prepared in the laboratory from mature August potatoes, with care to prevent contamination by organisms, dust, fumes, or water containing electrolytes. Pastes made by heating this starch in pure water could not be separated by centrifuging as described above. Experiments were then made to test the effect of adding small amounts of known electrolytes to the starch paste before centrifuging, and it was found that the addition of a very small amount of hydrochloric acid or sodium chloride sufficed to ensure a good separation. Since sodium chloride (at least in small amounts) is known to have no injurious effect upon amylolytic enzymes its use was decided upon, and in all subsequent centrifugal separations of 1% starch pastes enough sodium chloride was added to bring the concentration of salt in the final mixture to 0.001 *M*. When 2% starch pastes were to be separated a 0.002 *M* concentration of salt was employed.

The effect of varying the time and temperature of heating was studied in repeated experiments, in all of which the paste resulting from dispersion of the starch was separated by the centrifuge in the manner already described, the centrifugate filtered through filter paper covered with a thin layer of cotton, and the concentration of starch material in the filtered centrifugate was determined by evaporating and drying to constant weight at 80° *in vacuo*. These experiments showed that the bulk of the readily soluble material was extracted from the starch grains very quickly by water at 70 to 80°. When one part of starch suspended in 13 parts of cold water was poured into 87 parts of water heated sufficiently to give the entire mixture the desired temperature and containing sufficient salt to give the desired final concentration, thoroughly stirred for at least one minute until the viscosity no longer seemed to increase, and the paste

<sup>1</sup> There remains the possibility that by heating with water the less soluble component of the starch grain may be slowly changed into the more soluble— $\alpha$ -amylose into  $\beta$ -amylose as suggested by Meyer.

then centrifuged as promptly as practicable (within 10 minutes of the first exposure of the starch to the hot water) the concentration of amylose in the centrifugate was about the same as when the heating was continued for one hour. Prolonged heating (up to 30 hours) caused a very slow gradual increase in the amount of material going into the filtered centrifugate. Thus the concentration after heating at  $80^{\circ}$  for ten minutes to one hour averaged 0.20%; after 19 hours, 0.30%; after 30 hours, 0.35%.

In several cases the lower layer from the centrifugal separation was again treated with hot water and centrifuged a second and a third time, and the material thus extracted was compared as to amount and iodine reaction with the residual material and with the material of the first centrifugate. In this way it was found that the material brought into solution by repeated treatment with hot water, and, therefore, presumably the material which comes slowly into solution on prolonged heating with large excess of water, is different from that contained in the first centrifugate (original upper layer), and apparently consists of a mixture of the  $\beta$ -amylose which constitutes the chief solid of the upper layer and the  $\alpha$ -amylose which is the chief solid of the lower layer or residual gel.

To develop a given *intensity of blue color with iodine* requires from 13 to 18 times as much of the twice washed solids of the residual gel (crude  $\alpha$ -amylose) as is required of the solids of the original centrifugate (crude  $\beta$ -amylose); or, in other words, the solid matter of the  $\beta$ -amylose fraction had 13 to 18 times the blue-forming property<sup>1</sup> of the solids of the  $\alpha$ -amylose fraction, and the solids of the washings (second and third centrifugates) were of intermediate character.

No attempt was made to investigate the exact significance of these differences, which we recognize to depend to a considerable extent upon the amount of iodine arbitrarily chosen by Wohlgemuth for making such tests, because for the purposes of this investigation it was desired that the material going into the substrate should be as nearly homogeneous and as little changed from the form in which it exists in the natural starch as is possible. For these reasons it was decided to use in the separation of  $\beta$ -amylose only a short exposure of the starch to hot water as described above, centrifuging within 10 minutes and determining the solids in the centrifugate after filtering as already explained. Experiments at different temperatures indicated that the best results were obtained in heating at  $75^{\circ}$  in the preparation of 2%, or  $80^{\circ}$  in the preparation of 1% pastes.

*The viscosities as influenced by heating and by treatment with acid or alkali* also furnish evidence of a pronounced difference between the

<sup>1</sup> It is hardly necessary to say that in speaking of this as a property which helps to differentiate the two fractions, we do not mean to convey the impression of a definite chemical reaction in either case.

substances contained in the two layers separated by the centrifuge, the " $\beta$ -amylose" of our fractionation resembling the "amylose" of Gruzewska and of Samec in this respect and differing greatly from the  $\alpha$ -amylose fraction ("amylopectin").

Thus in an experiment in which the filtered  $\beta$ -amylose layer as obtained had a concentration of 0.4% and a viscosity of 1.13 the  $\alpha$ -amylose layer when diluted to the same concentration showed a viscosity of 1.18. On heating the  $\beta$ -amylose solution its viscosity was lowered to 1.03 after 5 minutes' and 1.02 after 20 minutes' boiling. Boiling the  $\alpha$ -amylose solution of the same concentration for 5 minutes raised its viscosity to 1.38, and heating for 1 hour in the autoclave at 125° increased it to 1.81; further heating in the autoclave caused decrease of viscosity—to 1.13 at the end of 2 hours' and 1.12 at the end of 3½ hours' heating at the same temperature.<sup>1</sup>

The addition of sufficient hydrochloric acid to give a concentration of 0.02 *N* did not change the viscosity of a  $\beta$ -amylose solution, and sodium hydroxide in equivalent concentration increased the viscosity only slightly. This is in accordance with the results of Samec<sup>2</sup> who finds that the viscosity of a starch solution (chiefly  $\alpha$ -amylose) is decreased by hydrochloric acid and increased by sodium hydroxide to a very marked extent while the viscosity of a solution of "amylose" ( $\beta$ -amylose) prepared by his modification of Gruzewska's method was not appreciably affected.

The two fractions into which starch is divided by the process above described and which, although not quantitatively free from each other, are for convenience referred to simply as  $\alpha$ - and  $\beta$ -amylose, also differ from each other in their behavior as regards *retrogradation*. We have had no evidence of retrogradation in any of our  $\alpha$ -amylose solutions, while the  $\beta$ -amylose solutions show the phenomenon to a pronounced degree, the more so the lower the temperature or the higher the concentration.

In an experiment to test this property  $\beta$ -amylose solutions of 0.6 and of 0.2% were allowed to stand in the refrigerator for three weeks and were then filtered. The filtrates contained only 0.04 and 0.037%, respectively. The completeness of this retrogradation is a further indication of the identity of this material with Gruzewska's amylose.<sup>3</sup> It seems not improbable that in ordinary starch pastes the  $\alpha$ -amylose may act as a protective colloid to the  $\beta$ -amylose. In all of the cases observed by us the retrogradation of the  $\beta$ -amylose has occurred more readily in the absence than in the presence of amylase, the enzymes being employed in purified form and low concentration. The suggestion that the amylase may exert a

<sup>1</sup> For discussion of effect of heat treatment upon viscosities of starch solutions see Harrison, *J. Soc. Dyers and Colorists*, April, 1911.

<sup>2</sup> Samec, *Koll. Beihefte*, 4, 132; 6, 32.

<sup>3</sup> *Compt. rend.*, 152, 785 (1911).

coagulating influence upon the substrate seems superfluous, at least as regards enzymes of the degree of purity used in these experiments. The phenomena observed by Maquenne and Roux and attributed by them to an amylocoagulase may possibly have been due to the digestion of  $\alpha$ -amylose and consequent removal of its protective effect upon the  $\beta$ -amylose.

In order to avoid retrogradation in our digestion experiments the solutions were autoclaved, allowed to cool to  $40^{\circ}$  and then promptly mixed with the enzyme solution, the activating salts being added at the same time (not mixed with the substrate in advance). Omission of such precautions is likely to result in cloudy digestion mixtures and delayed iodine end points.

The phosphorus content of the two fractions separated by the centrifuge was studied as a further indication of the relative amounts of  $\alpha$ - and  $\beta$ -amyloses and the extent to which they are differentiated by the procedure here used.

According to Samec, the phosphorus of starch is all contained in the  $\alpha$ -amylose ("amylopectin") portion. If, then, the centrifuge separates the  $\alpha$ - and  $\beta$ -amylose, the phosphorus should be found in the lower layer; but since in Northrop and Nelson's experiments<sup>1</sup> about one-tenth of the phosphorus escaped recovery it is possible that the  $\alpha$ - and  $\beta$ -amyloses might be separated by the centrifuge and still a fraction up to 10% of the original phosphorus might be found in the upper layer or diffused throughout the dispersion medium. In several experiments in which we have determined the phosphorus, the centrifugates (upper layers) constituting about 70% of the total volume have never contained more than about 2% of the total found. Our results are thus in harmony with the findings of Northrop and Nelson and with the view that  $\alpha$ - and  $\beta$ -amylose ("amylopectin" and "amylose") are separable by heating with water and centrifuging as here described.

The amounts of phosphorus found in the  $\beta$ -amylose fraction are but little, if any, above the limits of experimental error, and for most purposes might be regarded as negligible, but since the concentration of solids in this layer is only about 0.20% the percentage of phosphorus in the solids is about one-tenth as high for this fraction as for the whole starch, so that it seemed desirable to ascertain if possible whether the phosphorus of the  $\beta$ -amylose layer were present merely as diffusible phosphate or in the form of  $\alpha$ -amylose or other non-diffusible material.

The centrifugates ( $\beta$ -amylose layers) from several experiments were saved and united, a portion of the solution reserved and the remainder dialyzed in a collodion bag against 5 to 8 times its volume of redistilled water for 8 days, the water being changed every day. A portion of the

<sup>1</sup> THIS JOURNAL, 38, 472 (1916).

centrifuge residue ( $\alpha$ -amylose layer) was diluted to a similar concentration and dialyzed under the same conditions. With the kind assistance of Dr. I. Greenwald of the Harriman Research Laboratory, the phosphorus content of these solutions was determined nephelometrically by precipitating as strychnine phosphomolybdate according to the method of Pouget and Chouchak.<sup>1</sup> The  $\beta$ -amylose layer showed before dialysis 0.00002% and after dialysis 0.00001% of phosphorus; the  $\alpha$ -amylose layer after dilution to corresponding concentration of solids showed 0.00195% before, and 0.00180% after dialysis. Thus the eight-day dialysis had removed half of the phosphorus of the  $\beta$ -amylose layer and somewhat less than one-tenth of that of the  $\alpha$ -amylose layer. Calculating the phosphorus in percentage of the starch solids present it is found before dialysis to constitute 0.068% of the  $\alpha$ -amylose fraction and 0.010% of the  $\beta$ -amylose fraction, or about one-seventh as much in the latter case as in the former. If the phosphorus were assumed to be present only in the form of  $\alpha$ -amylose it would follow that the amylose of the upper layer from the centrifuge is about one-seventh  $\alpha$ -amylose and six-sevenths  $\beta$ -amylose; but since at least half of the phosphorus of this fraction is dialyzable it appears probable that well over nine-tenths of the starch material in the upper layer from the centrifuge tube is  $\beta$ -amylose (using this term to designate the phosphorus-free fraction of starch which gives a pure blue reaction with iodine). From the comparison of iodine color reactions and solubilities it also appears probable that the starchy material of the lower layer after separation and two washings in the centrifuge is at least nine-tenths  $\alpha$ -amylose.

Thus it appears that by the method of regulated dispersion and centrifugal separation here described it is feasible to divide potato starch into two fractions, one of which is more than nine-tenths  $\alpha$ -amylose and the other more than nine-tenths  $\beta$ -amylose. If amylases behave differently toward  $\alpha$ - and  $\beta$ -amylose it should be possible to study their differences in behavior by experiments in which these two fractions are used side by side as substrates for the action of the enzyme. The data recorded below are typical of those which we have obtained in several series of comparative experiments of this sort.

#### Experiments with Enzymes.

In the experiments with enzymes recorded in this paper we have used each enzyme in the presence of its optimum concentration of salt and phosphate as determined in previous work in this laboratory.

Except as different enzymes with their appropriate activators were used, the only variable factor was the nature of the substrate. All digestions were conducted at 40° with all the precautions as to purity of reagents and water used, and accurate control of time and temperature,

<sup>1</sup> *Bull. soc. chim.*, [4] 5, 104 (1909); 9, 649 (1911).

which have been described in previous papers.<sup>1</sup> The enzyme hydrolysis of four potato starch substrates— $\alpha$ - and  $\beta$ -amyloses, Lintner soluble starch, and whole starch autoclaved—has been studied at two concentrations of substrate, 0.16% and 0.5%. For the sake of brevity only the latter will be described.

**Preparation of Substrates.**—The  $\alpha$ -amylose substrate was prepared by centrifuging a 1% starch paste made at 85° in a concentration of 0.001 *M* sodium chloride as previously described. The supernatant  $\beta$ -amylose layer was decanted off and an equal volume of hot 0.001 *M* sodium chloride stirred into the  $\alpha$ -amylose layer and this again centrifuged. This washing was repeated and the residue then diluted to the original volume and this solution (about 0.8%) heated in autoclave at 125° for 2½ hours. The exact concentration was then determined by evaporating a portion *in vacuo* at 80°. When about to start an experiment, this solution was sufficiently diluted with water so that when mixed with the activator and enzyme solutions the desired final concentration of 0.5% substrate would be obtained.

The  $\beta$ -amylose substrate was prepared by centrifuging a 2% starch paste prepared at 75° containing sodium chloride in 0.002 *M* concentration. The supernatant liquid from the centrifuge tube was filtered through paper covered with a thin layer of absorbent cotton. About 170 cc. of 0.4% filtered  $\beta$ -amylose solution were obtained from 400 cc. of 2% starch paste. Two such filtrates were usually united. A portion of this solution was evaporated *in vacuo* at 80° to determine the exact concentration of  $\beta$ -amylose and a larger measured volume (sufficient for the experiment contemplated) was concentrated by evaporation to about 0.8%, autoclaved in the same manner as the  $\alpha$ -amylose solution and finally brought exactly to the desired concentration.

"Autoclaved starch" was prepared by heating an 0.8% starch paste in the autoclave as described under  $\alpha$ -amylose, and then bringing to the proper concentration.

"Soluble starch" (Lintner) was "dissolved" by boiling with water for 10 minutes and was not heated in the autoclave.

The initial reducing power of each substrate was determined and this value subtracted from that found in the digestion experiments.

Each digestion experiment was started by measuring the enzyme solution into a flask and pouring into it the proper volumes of substrate solution and of the solution of activating salts so that the concentration of substrate in the final digestion mixture was exactly 0.5%. The substrate and activator solutions were measured at 40° and this temperature was maintained throughout the experiment, portions being withdrawn by

<sup>1</sup> THIS JOURNAL, 32, 1073, 1087; 33, 1195; 35, 1617; 37, 623.

pipet from time to time without removing the main solution from the thermostat.

The four experiments of a set were started at intervals of one minute so that portions of each might be withdrawn in succession after exactly equal digestion periods. Each measured portion as withdrawn was at once delivered into a flask containing mixed Fehling solution, and the reducing sugars determined at once, following the procedure described by Sherman, Kendall and Clark<sup>1</sup> and calculating the result as maltose by means of Defren's table.<sup>2</sup> In order to simplify the tabular statement and comparison of the results, the weights of reduced copper and the corresponding weights of maltose are omitted and only the maltose as calculated in terms of the amount theoretically obtainable from the substrate and the corresponding velocity constant are printed. Since it has been shown<sup>3</sup> that even purified amylases may form appreciable amounts of glucose as well as maltose, it is possible that the figure for maltose calculated from the reduction of Fehling solution may, in prolonged digestions or under special conditions of enzyme or substrate, exceed the theoretical yield.

**Action of Pancreatic Amylase.**—The four substrates above described were quantitatively compared as regards their digestion by pancreatic amylase, first in the form of a high grade commercial pancreatin (Pancreatin 6) and then in the form of a highly purified laboratory preparation (Preparation 59). The results are shown in Tables II and III, respectively.

TABLE II.—HYDROLYSIS OF DIFFERENT SUBSTRATES BY COMMERCIAL PANCREATIC AMYLASE (PANCREATIN 6).

Time.	Soluble starch.		Autoclaved starch.		$\alpha$ -Amylose substrate.		$\beta$ -Amylose substrate.	
	Maltose in terms of theory.	$k \times 10^3$ .	Maltose in terms of theory.	$k \times 10^3$ .	Maltose in terms of theory.	$k \times 10^3$ .	Maltose in terms of theory.	$k \times 10^3$ .
30 min.....	4.3	63	4.3	63	4.6	67	5.2	77
60 min.....	8.4	63	8.5	64	7.7	58	10.7	81
90 min.....	12.5	64	13.0	67	11.2	57	15.2	79
120 min.....	16.2	64	17.5	69	14.9	58	20.4	82
150 min.....	20.0	64	21.0	68	18.4	58	25.6	85
180 min.....	23.0	63	24.4	69	21.2	57	31.3	91
210 min.....	26.7	64	28.1	68	24.4	57	35.6	91
240 min.....	29.5	63	31.1	67	26.9	56	39.9	92
6 hours.....	38.6	58	40.2	62	35.6	53	52.4	91
18 hours.....	56.2	33	58.0	34	52.8	30	75.2	56
24 hours.....	59.3	26	61.2	28	56.9	25	77.5	45

<sup>1</sup> THIS JOURNAL, 32, 1072 (1910).

<sup>2</sup> *Ibid.*, 18, 749.

<sup>3</sup> Sherman and Punnett, *Ibid.*, 38, 1877 (1916).

\* From the formula  $(1/l \log a/a - x = k)$  in which  $l$  = time in minutes;  $a$  = the amount of maltose theoretically obtainable (starch  $\times 1.05$ ) and  $x$  = maltose found at time  $l$ .



TABLE III.—HYDROLYSIS OF DIFFERENT SUBSTRATES BY PURIFIED PANCREATIC AMYLASE (PREPARATION 59).

Time.	Soluble starch.		$\alpha$ -Amylose substrate.		$\beta$ -Amylose substrate:	
	Maltose in terms of theory. %	$k \times 10^3$ .	Maltose in terms of theory. %	$k \times 10^3$ .	Maltose in terms of theory. %	$k \times 10^3$ .
30 min.....	4.4	65	4.2	62	6.1	91
60 min.....	10.8	83	7.5	56	11.3	87
90 min.....	13.1	67	11.4	58	16.8	86
120 min.....	17.0	67	14.9	58	22.6	93
150 min.....	21.9	71	18.0	57	28.2	96
180 min.....	25.7	72	21.0	57	33.7	99
210 min.....	28.8	70	24.0	57	38.7	101
240 min.....	31.5	68	26.5	56	43.2	102
6 hours.....	39.0	59	34.8	51	55.0	96
24 hours.....	59.4	27	55.1	24	84.5	56

It will be seen that under the action of pancreatic amylase, whether in commercial or purified form, the yield of reducing sugar is higher for the  $\beta$ -amylose than for the  $\alpha$ -amylose fraction at each of the stages at which the digestion mixture was tested, the difference becoming greater as the digestion proceeds. The amount of enzyme here used was small in order that the progress of the reaction might be slow enough to be followed experimentally through the earlier stages. Under these conditions, at the end of 24 hours, when the last of the digestion mixture was withdrawn for testing, the reaction was still in progress and the yield of maltose had reached in the two series of experiments, respectively, only 56.9 and 55.1% of theoretical in the  $\alpha$ -amylose, and 77.5 and 84.5% in the  $\beta$ -amylose fraction.

Since each of the successive reactions by which maltose is formed is an hydrolysis taking place in water solution, and, therefore, essentially a unimolecular reaction, and it is the catalytic effect of the enzyme which causes these reactions to proceed at a measurable rate, it follows that the speed of formation of maltose may be expressed in terms of  $k$  of the unimolecular reaction formula ( $1/t \log a/a - x = k$ ) and that (under a given set of conditions as in either one of the two sets of experiments here described) the magnitude of  $k$  at any given stage in the experiment may be regarded as an indication of the efficiency with which the formation of maltose is catalyzed at that stage. Constancy of  $k$  from the beginning of the experiment until a practically theoretical yield of maltose is obtained would indicate that the group of hydrolyses which produce maltose (that of starch and of each of the resultant dextrins) is equally catalyzed by the enzyme throughout; whereas if the digestion yields at any stage a dextrin which is less readily hydrolyzed by the enzyme, the value of  $k$  must diminish. A fall in the value of  $k$  may, therefore, serve as an indication of the formation of a "resistant dextrin." When equal amounts of the same enzyme act on equal amounts of different sub-

strates under identical conditions, a comparison of the values for  $k$  may indicate an earlier or a larger production of "resistant dextrin" from one substrate than from the other.

The data in Table II show in all cases a decided diminution of the velocity of reaction (expressed as value of  $k$ ) between the 6th and the 18th hour. Comparing the yields of maltose from the different substrates at these periods it is plain that the decrease in value of  $k$  began at a lower yield of maltose in the  $\alpha$ -amylase than in the  $\beta$ -amylase fraction, indicating that the former yields more of the relatively resistant dextrin than the latter, or that its dextrin is more resistant than the corresponding dextrin from  $\beta$ -amylase. Lintner soluble starch and autoclaved whole starch gives intermediate results, but approach the behavior of  $\alpha$ -amylase more closely than that of  $\beta$ -amylase as is consistent with the other evidence that they consist much more largely of the former than of the latter.

Similar comparison of the data obtained in experiments with other amylases described below will show that the stage of digestion at which the value of  $k$  begins to diminish depends upon the enzyme as well as the substrate but that in all cases the indications of "resistant dextrin" are much more pronounced in the  $\alpha$ -amylase than in the  $\beta$ -amylase fraction.

There are, of course, many causes which may contribute to the slowing of the reaction as the hydrolysis proceeds, such as the destructive action of water upon the enzyme, inactivation of enzyme by combination with hydrolytic products, etc. Without entering into discussion of such factors here, it may be pointed out that the arrangement of these experiments was such that any distinctly different behaviors of  $k$  in experiments recorded in any one table (such as discussed in the above paragraph referring to Table II) may be interpreted as due to some difference in the substrate or its hydrolytic products. The general relations noted from the data of Table II will be seen to hold true for those of Table III also.

**Action of Malt Amylase.**—Parallel tests upon the  $\alpha$ - and  $\beta$ -amylase substrates at 0.5% concentration were made with a freshly prepared malt amylase preparation of a diastatic power of 957<sup>1</sup> prepared essentially as described in previous papers from this laboratory, but precipitated at a concentration of alcohol slightly higher than usual, *viz.*, 65–70%; and also with a preparation purified in the usual way and in which the final active precipitate was obtained at a somewhat lower concentration of alcohol, *i. e.*, Preparation 151, precipitated at 57.5 to 65% alcohol, diastatic power 1240.<sup>1</sup> Except for the kind and amount of enzyme used, the experiments were in all respects similar to those with pancreatic amylase just described. The results with these two malt amylase preparations are given in Tables IV and V, respectively.

<sup>1</sup> Expressed on the scale used since 1910 (Sherman, Kendall and Clark, THIS JOURNAL, 32, 1073.

TABLE IV.—HYDROLYSIS OF  $\alpha$ - AND  $\beta$ -FRACTIONS OF STARCH BY MALT AMYLASE PRECIPITATED AT 65-70% ALCOHOL.

Time.	$\alpha$ -Amylose substrate.			$\beta$ -Amylose substrate.		
	Maltose in terms of theory.	%.	$k \times 10^3$ .	Maltose in terms of theory.	%.	$k \times 10^3$ .
30 min.....	10.2		156	5.6		84
60 min.....	19.2		154	10.8		82
90 min.....	26.4		148	15.5		81
120 min.....	32.2		141	22.1		90
150 min.....	36.7		131	27.4		93
180 min.....	40.3		124	32.5		95
210 min.....	43.2		117	36.4		94
240 min.....	45.8		110	39.8		92
6 hours.....	50.4		84	53.2		91
24 hours.....	58.1		26	82.2		52

TABLE V.—HYDROLYSIS OF DIFFERENT SUBSTRATES BY MALT AMYLASE PREPARATION 151, POWER 1240.

Time.	Soluble starch.		Autoclaved starch.		$\alpha$ -Amylose substrate.		$\beta$ -Amylose substrate.	
	Maltose in terms of theory.	%.	Maltose in terms of theory.	%.	Maltose in terms of theory.	%.	Maltose in terms of theory.	%.
30 min.....	29.2	499	26.6	448	28.3	482	19.8	321
60 min.....	48.4	477	44.0	418	46.8	462	38.8	355
90 min.....	58.5	424	54.9	384	53.6	401	56.3	399
120 min.....	62.2	352	59.8	330	57.9	313	70.0	436
150 min.....	64.3	298	63.6	292	60.3	267	81.8	493
180 min.....	65.2	255	65.8	258	61.6	231	91.3	590
210 min.....	66.5	226	67.7	234	62.4	202	97.6	766
240 min.....	68.2	208	69.5	216	62.7	179	98.7	785
270 min.....	68.7	188	70.4	198	63.1	162	99.0	748

Comparison of the data of Tables IV and V shows that the purified malt amylase preparations exert in the earlier stages of the digestions a greater saccharifying action upon the  $\alpha$ -amylose than upon the  $\beta$ -amylose substrate, while in the later stages the  $\beta$ -amylose shows the greater yield of maltose.

The notable feature of the action of malt amylase upon the  $\beta$ -amylose substrate is the striking way in which the speed of formation of maltose is maintained as compared either with the action of this enzyme upon other substrates or the action of other amylases upon this substrate. In the experiment with a small amount of enzyme (Table IV) the values of  $k$  show no decrease until the formation of maltose is nearly complete, and with a larger amount of enzyme (Table V) the values of  $k$  increase, the time curve being substantially linear, up to a nearly theoretical yield of maltose. This may be expressed as a maintenance throughout the process of the linear relationship usually noted in the earlier stages of such

hydrolytic enzyme actions. The explanation is probably to be found in accumulation of hydrolyzable products and the efficiency with which the enzyme catalyzes the later of the series of consecutive hydrolyses by which maltose is produced. Simultaneous effective catalysis of the successive steps in the process would naturally tend to increase the value of  $k$  as computed from the simple unimolecular reaction formula and this tendency will be further augmented by the fact that the velocity of the reaction during the later stages is compared with that shown at the beginning of the process where in the case of this enzyme the  $\beta$ -amylose is hydrolyzed less readily than are the other substrates. With the small amount of enzyme used in the experiments of Table IV this tendency toward a rise in the value of  $k$  suffices merely to balance the factors which tend toward a loss or inactivation of the enzyme; whereas with the larger concentration of enzyme in the experiments of Table V the latter factors are not appreciable and the rise in value of  $k$  becomes very pronounced. Thus the detailed study of the course of the hydrolysis under the influence of a precipitated malt amylase of this character brings out a new difference in behavior between the  $\alpha$ - and  $\beta$ -fractions of the starch.

In all cases the saccharification of the substrate had proceeded to a much higher yield of maltose from  $\beta$ -amylose than from  $\alpha$ -amylose when the concentration of enzyme was such as would be used in determinations of diastatic power and the experiments were sufficiently prolonged to produce maltose up to or beyond half the theoretical yield.

When the amount of enzyme used is much larger the same result may be obtained in a short time as shown in Table VI.

TABLE VI.—HYDROLYSIS OF  $\alpha$ - AND  $\beta$ -SUBSTRATES WITH A RELATIVELY LARGE AMOUNT OF PURIFIED MALT AMYLASE (PREPARATION 153).

Time.	Reducing sugar as percentage of theoretical yield of maltose.	
	From $\alpha$ -amylose substrate.	From $\beta$ -amylose substrate.
20 min.....	54.5	72.4
40 min.....	67.1	100.0
60 min.....	68.7	100.2
154 min.....	71.4	100.8

Evidently even a relatively large amount of enzyme does not readily hydrolyze the material which remains in the  $\alpha$ -amylose fraction after two-thirds of the theoretical amount of maltose has been produced, while in the  $\beta$ -amylose fraction under the influence of the same amount of enzyme the hydrolysis runs rapidly to a theoretical yield of maltose. It thus appears that the "resistant dextrin" emphasized by many previous investigators as a product of the action of malt amylase upon starch is derived only from the  $\alpha$ -amylose and not from the  $\beta$ -amylose fraction. After the theoretical yield of maltose from  $\beta$ -amylose has been obtained, the increase in reducing power is exceedingly slow, indicating that even

this amount of purified malt amylase has only a slight hydrolytic action upon maltose.

The rapid digestion of  $\beta$ -amylose in this experiment explains the statement of Maquenne and Roux<sup>1</sup> to the effect that "amylose" ( $\beta$ -amylose) is immediately hydrolyzed to the theoretical amount of maltose by malt, since in their experiments very liberal amounts of malt extract were used.

**Action of the Amylase of *Aspergillus Oryzae*.**—Experiments upon Lintner soluble starch, autoclaved whole starch, and  $\alpha$ - and  $\beta$ -amylose substrates all at 0.5% concentration have been carried out as described above with the amylase of *Aspergillus oryzae* prepared in this laboratory by Dr. A. P. Tanberg from takadiastase by the purification method described elsewhere.<sup>2</sup> The preparation here used was No. 22b having a diastatic power of 502 as expressed on the scale in use in this laboratory. This corresponds to a Lintner value of about 750. The Wohlgemuth value of this preparation was about 1,000,000.

The results obtained with this amylase preparation are shown in Table VII.

TABLE VII.—HYDROLYSIS OF DIFFERENT SUBSTRATES BY AMYLASE OF *ASPERGILLUS ORYZAE* (PREPARATION 22b).

Time.	Soluble starch.		Autoclaved starch.		$\alpha$ -Amylose substrate.		$\beta$ -Amylose substrate.	
	Maltose in terms of theory.	$k \times 10^5$ .	Maltose in terms of theory.	$k \times 10^5$ .	Maltose in terms of theory.	$k \times 10^5$ .	Maltose in terms of theory.	$k \times 10^5$ .
30 min. ....	10.5	161	11.9	183	12.2	188	14.3	224
60 min. ....	19.8	159	23.0	189	23.4	193	28.5	243
90 min. ....	29.8	171	32.7	191	33.3	195	41.3	257
120 min. ....	35.1	156	39.0	179	39.5	182	51.4	261
150 min. ....	40.0	148	45.7	176	43.4	165	58.9	258
180 min. ....	43.8	139	49.7	167	47.5	155	64.1	247
210 min. ....	46.7	130	53.6	159	50.4	145	67.7	234
240 min. ....	48.8	120	55.6	147	53.2	138	70.0	218
360 min. ....	53.5	92	63.4	121	59.4	108	75.0	168
24 hours. ....	62.8	29	75.4	42	...	...	...	...

From the data given in Table VII together with the results of two other series not reproduced here, it may be concluded that the purified amylase of *Aspergillus oryzae* exerts essentially the same saccharogenic action upon Lintner soluble starch, autoclaved whole starch and the  $\alpha$ -amylose substrate, while upon the  $\beta$ -amylose substrate it shows a greater saccharogenic action at whatever stage in the digestion the results be compared. The speed of hydrolysis was not so well sustained in this case as with the other amylases; even in the case of the  $\beta$ -amylose substrate there is here a falling off of the rate of saccharogenic action before the reducing

<sup>1</sup> *Compt. rend.*, 140, 1303 (1905).

<sup>2</sup> Sherman and Tanberg, *THIS JOURNAL*, 38, 1638 (1916).

sugar reaches the equivalent of 70% of a theoretical yield of maltose, notwithstanding the fact that this amylase is more active in hydrolyzing maltose to glucose than is either pancreatic or malt amylase. This property is doubtless related to the high ratio of amyloclastic to saccharogenic activity of this enzyme which will be considered in the next section.

**Relation of Amyloclastic to Saccharogenic Action.**—In many of the experiments comparing the different substrates the time of disappearance of the blue or violet reaction with iodine was noted and the amount of maltose which had been formed at this time was found either by direct determination or by interpolation from the determinations of reducing power made at known intervals in the course of the same experiment. While no great accuracy is to be expected of such attempts to determine the stage of digestion at which the starch disappears, as judged by the iodine test, yet they permit comparisons of the amyloclastic and saccharogenic activities which at least are not open to such gross discrepancies as may arise when comparisons are made between saccharogenic powers as ordinarily determined and amyloclastic powers determined by the Wohlge-muth method.<sup>1</sup>

In the case of pancreatic amylase the present experiments show with each of the four substrates a maltose production from 35 to 50% of the theoretical at the point of disappearance of the blue or violet color reaction with iodine. Allowing for the difference in experimental conditions this may be considered as a confirmation for all four substrates of the ratio of about 2 : 1 previously established for the action of pancreatic amylase upon Lintner soluble starch.

In the experiments with the amylase of *Aspergillus oryzae* the iodine end point occurred at a much earlier stage in the saccharogenic action, usually when from 20 to 30% of the theoretical yield of maltose had been produced. This high ratio of amyloclastic to saccharogenic activity and the relatively early decrease in velocity of maltose formation noted above are both indications that this amylase exerts a more pronounced catalytic effect upon the earlier than upon the later of the hydrolyses involved in the transformation of starch through dextrins into maltose.

Malt amylase, on the other hand, is, as shown by the data of Tables IV and V, an active catalyst of sugar production even in the relatively advanced stages of the process; and apparently it does not correspondingly catalyze the complete disruption of the material to which the iodine test is due since the iodine end point is found only at a much more advanced stage of sugar production with this than with either of the other amylases. When acting upon Lintner soluble starch, autoclaved whole starch, or the  $\alpha$ -amylose substrate the malt amylase preparations caused disap-

<sup>1</sup> For a discussion of these discrepancies see Sherman and Schlesinger, *This JOURNAL*, 35, 1784-90.

pearance of the iodine test only when from 65 to 80% of the theoretical yield of maltose had been produced; and when acting upon the  $\beta$ -amylose substrate, only when the maltose production had reached 85 to 95%. Thus the "delayed iodine end point" remarked in previous papers as characteristic of the hydrolyses induced by purified malt amylase, is found to be a noteworthy feature of its action upon both  $\alpha$ - and  $\beta$ -amylose.

### Summary.

Dispersions of commercial potato starch in water or of purified potato starch in water containing a small amount of electrolyte (sodium chloride) have been separated by centrifugal force into a heavier, very viscous, opalescent layer containing the more abundant, less soluble component of the starch (Meyer's  $\alpha$ -amylose, Maquenne's amylopectin), and a lighter, limpid solution containing the less abundant, more soluble component (Meyer's  $\beta$ -amylose, Maquenne's amylose).

In designating these two chief components (or derivatives) of starch the terminology of Meyer is preferred to that of Maquenne, not only on grounds of priority but also as being much more appropriate in view of our present knowledge of the relative abundance of the two components, their properties as compared with the typical properties of starch, and their behavior toward the amylases.

The centrifugal method here described does not completely separate either component from the other but affords a means of approximate separation in which the danger of contamination, denaturization, or retrogradation is minimized and which is well adapted to the study of the effects of the different amylases.

Pancreatic amylase both in commercial and in highly purified form produced reducing sugar more rapidly from  $\beta$ -amylose than from  $\alpha$ -amylose, autoclaved starch, or Lintner soluble starch, the last three giving very similar results when used as substrate for this enzyme. Not only does the  $\beta$ -amylose substrate show larger yield of maltose at each of the various time intervals tested, but the initial speed of hydrolysis is better maintained with this substrate than with either of the others.

Purified malt amylase shows in the earlier stages of its action a somewhat greater yield of maltose from  $\alpha$ - than from  $\beta$ -amylose. As the digestion proceeds, the saccharogenic action of this enzyme upon  $\alpha$ -amylose becomes slower while its action upon  $\beta$ -amylose is well sustained so that in cases in which the hydrolysis proceeds to the production of more than half the theoretical yield of maltose, the final result shows a greater saccharogenic action upon  $\beta$ - than upon  $\alpha$ -amylose. The results obtained upon autoclaved starch and Lintner soluble starch are very similar to those found with  $\alpha$ -amylose.

The amylase of *Aspergillus oryzae* digests Lintner soluble starch, autoclaved whole starch and  $\alpha$ -amylose at about equal rates, and  $\beta$ -amylose

at a somewhat higher rate. Its action upon the  $\beta$ -amylose substrate is, however, not so well sustained as that of pancreatic or malt amylase. This relatively early falling off in the speed of sugar formation together with the high ratio of amylolytic to saccharogenic power indicate that this amylase is a more active catalyst of the earlier than of the later stages of the hydrolysis.

Contrasting the action of comparable amounts of the three different amylases it appears that they catalyze the successive stages of the hydrolysis of  $\beta$ -amylose and its products at relatively different velocities. The time curve for pancreatic amylase is practically logarithmic up to the production of about three-fourths the theoretical amount of maltose while beyond this point the reaction proceeds at a lower velocity. Compared with this result, the catalytic effect of the amylase of *Aspergillus oryzae* is more pronounced in the earlier and less pronounced in the later stages, while purified malt amylase is relatively less efficient in the earlier stages but catalyzes the later stages more efficiently.

In the digestion of  $\alpha$ -amylose all of the amylases showed more pronounced catalytic effect upon the earlier than upon the later stages of the digestion. Starch pastes made at low temperatures ( $65-80^{\circ}$ ), autoclaved starch, and Lintner soluble starch all resemble the  $\alpha$ -amylose rather than the  $\beta$ -amylose substrate in their behavior toward all three amylases, doubtless because  $\alpha$ -amylose is the chief component of all these forms of starch.

The separation of starch into its  $\alpha$ - and  $\beta$ -fractions made possible a more satisfactory study of the course of the amylase hydrolyses because of the greater homogeneity of the new substrates. All the data pertaining to the earlier stages of these hydrolyses indicate that Lintner soluble starch is well adapted to its purpose as substrate for testing the activities of the different amylases and that its use leads to conservative estimates of the diastatic powers of purified preparations.

Tested upon any of the four substrates here studied, the three amylases show distinctly different ratios of amylolytic to saccharogenic powers.

LABORATORY OF FOOD CHEMISTRY,  
NEW YORK, N. Y.

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### CORRECTIONS.

Page 1366, line 7 from bottom: after the words "to  $170^{\circ}$ " insert "with aniline."

In the article by C. E. Hudson in the August number of THIS JOURNAL (p. 1572, line 22) the specific rotation of trehalose octacetate in chloroform should be " $+162^{\circ}$ " instead of " $-162^{\circ}$ ."

On page 1569, line 11 from the bottom, "melibiose" should be "gentiobiose."



## NEW BOOKS.

**Practical Physical Chemistry.** By FRANCIS W. GRAY. Lecturer in Charge of the Physical Chemistry Department, Aberdeen University. XVI and 211 pp. 61 figs. Macmillan and Co. New York. Price, \$1.25.

This is an excellent little manual for a first course in laboratory work in physical chemistry. The thirty-nine "exercises" include all the methods ordinarily given in such a course. They are arranged in chapters or groups, each group being preceded by a brief, clear statement of the fundamental principles involved in the experiments which follow. The laboratory directions are precise, adequate, and accompanied by well executed and intelligible diagrams. The author lays stress on the fact that he has so planned that no one exercise requires more than the usual period of two or three hours for its completion, and this is a good feature. The first thirty-five pages are devoted to a valuable discussion of "Accuracy" and "Errors;" the last seventeen to "Tables" and "Useful Data."

The style is uniformly concise and lucid, producing a most favorable impression on the reader, but occasionally one feels that this brevity is carried a trifle too far, and that a little more explanation in the text would be desirable. It would forestall a good many questions which will inevitably arise in the minds of those new to the work. The only thing which disturbed the enjoyment of the reviewer in reading this book was the appearance, four or five times, of the unfamiliar word "dissolecule," meaning molecular weight. Additions to the already unnecessarily long list of "special" words should be made only when it is unavoidable. But one small blemish can readily be forgiven among so much that is admirable.

S. LAWRENCE BIGELOW.

**A Laboratory Course in Organic and Physiological Chemistry.** By A. P. LOTHROP, PH.D., Assistant Professor of Physiological Chemistry, Queens University. R. Uglow & Co., Kingston, Ontario. 1915. 83 pp.

The rapid development of physiological chemistry in the past few years is indicated among other things by the large number of laboratory manuals which are appearing. This indicates that the science is still in a state of flux, that the teaching has not yet been standardized, or at any rate that there is as yet no generally accepted opinion as to what should be covered in the course and how it should be taught. Each teacher makes his own laboratory course. Of the several such manuals which have appeared in the past year, this is one of the simpler and older fashioned. It contains some simple experiments in organic chemistry and following these the ordinary, simpler tests for special substances and methods of examination of certain tissues and the urine. The experiments are clearly described, the directions are printed on one side of the page only leaving space for the recording of the results in the book itself, and the student is generally not told what to observe but only to write down

what he sees. There is no explanation of any of the reactions or observed facts, the author evidently expecting that this will be supplied by the text-book or brought out in recitation. Only one or two quantitative methods are given for the examination of the urine.

The reviewer is of the opinion that for modern, first-class medical schools, in which organic chemistry is required for entrance, the organic chemistry experiments are superfluous. If these were left out, the book could be much improved, without lengthening it, by the introduction of some of the modern quantitative chemical methods for the examination of blood and the secretions of the body. The book represents about what was required in most medical schools ten to fifteen years ago.

A. P. MATHEWS.

THE JOURNAL  
OF THE  
American Chemical Society

with which has been incorporated the

American Chemical Journal  
(Founded by Ira Remsen)

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THE OSMOTIC PRESSURE OF SUCROSE SOLUTIONS AT 30°.<sup>1</sup>

By J. C. W. FRAZER AND R. T. MYRICK.

Received June 17, 1916.

Introduction.

The purpose of this work was to modify the method of measuring osmotic pressures developed by Morse and Frazer; so that it would be applicable to a study of concentrated solutions and, possibly, to solutions of electrolytes. This demands two things: first, the semipermeable membrane must have greater strength in order to withstand the greater pressures and, second, it must be able to establish equilibrium between the "escaping tendencies" of the solvent on the two sides of the membrane much more quickly, so that a measurement may be secured before the ions of electrolytes have time to destroy the colloidal nature of the membrane. Greater strength and greater speed of action have both been secured and the efficiency of the method for the measurement of the osmotic pressure of concentrated solutions, tested and proven. Its applicability to electrolytes is an unsettled question, but the prospects are every encouraging. It is planned to make a thorough trial of this in the near future.

The method<sup>2</sup> of measuring osmotic pressure developed in this laboratory is in brief as follows: A semipermeable membrane of copper ferro-

<sup>1</sup> This work has been aided by the Carnegie Institution of Washington, D. C.

<sup>2</sup> *Pub. Carnegie Inst.*, No. 198.

cyanide is electrolytically deposited on the inside and in the pores, near the inner surface of a clay cell. The solution to be measured is placed inside of this cell and a manometer is tightly fastened in its mouth. The cell is then immersed in the solvent and the pressure, developed by the passage of solvent through the membrane into the solution, is registered on the manometer.

The modification of this method, which it is the purpose of this article to describe, is essentially a reversal of the above-mentioned process. The membrane is deposited on, and in the pores near, the outer surface of the cell. The cell is fastened inside of a hollow bronze cylinder to which the manometer is attached. The solution to be measured is placed inside of the cylinder around the clay cell, the solvent being placed inside of the latter. This position of the membrane is similar to that used by Berkeley and Hartley.<sup>1</sup> However, these investigators applied mechanical pressure to the solution until equilibrium was established, while in the present instance the solution developed its own pressure as in the apparatus used heretofore in this laboratory.

#### Description of the Apparatus.

The details of construction are shown in the accompanying diagram (Fig. 1) in actual size. M is the clay cell with the membrane of copper ferrocyanide K deposited on its exterior. This extends only as far, as indicated by the heavy line K, the neck and shoulder of the cell being glazed to ensure tight joints. J is the bronze cylinder into which the cell is fastened by means of the plug P. The latter has three legs upon which the apparatus stands and which serve as a means of screwing the plug into the cylinder. N is a thick rubber washer and O is a piece of commercial "Rainbow Packing," about a millimeter and a half thick. This packing gives perfect satisfaction, while ordinary rubber will not withstand higher pressures. At all other joints, N, G, H, the packing is surrounded on all sides so it can not get away, hence in these places the softer rubber washers answer very well. In fact, it is desirable to have N and G thick (about 4 mm.) and soft so that initial pressure may be secured by their compression.

R is a glass U-tube held in the mouth of the cell by means of the rubber stopper Q. This is simply to keep the solvent L up in the cell and yet leave it open to the atmosphere. I is the solution to be measured. E is the manometer attachment and is fastened onto the cylinder by means of nut F, G being a thick rubber washer described above. A is a piece of capillary glass tubing to which the manometer is sealed. The square shoulder at the lower end of A is secured by sealing on to a piece of tubing, of the size desired for A, another piece, having somewhat larger external dimensions. The joint is kept soft and the glass allowed to flow together

<sup>1</sup> *Trans. Roy. Soc., (A)* 206, 481 (1906).

until a considerable enlargement is secured, the internal diameter being kept of original size by careful blowing. After cooling, the larger piece of tubing is cut off close to the enlarged joint. A is then mounted in the lathe and the enlarged end ground to the desired size and shape. The grinding is done with carborundum dental wheels mounted on the lathe carriage and rotated at a high speed by a small electric motor. In this manner the lower end of A is made to fit accurately into the lower end of E, as shown in the diagram. To hold A in position, B is sealed onto A by means of sealing wax (Khotinsky) and after putting D into position, C is screwed onto B. Now it will be seen that by turning D to the left, A is raised and held tightly in position in E against the washer H. By turning D to the right, A is lowered and excess solution is allowed to escape. This method of joining glass and metal is of general application and has proven most satisfactory. Such a joint will hold tight under any pressure which will not actually break the glass.

Several points of advantage over the old type of cell deserve especial mention. In the first place the clay cell will withstand far greater pressure exerted upon its exterior than upon its interior, as would be expected from a consideration of the principles of arch construction. Secondly, the membrane itself is made stronger, for the pressure tends to force it farther into the pores and so compresses it, making it more firm and compact. With the membrane on the inside of the cell the pressure of the inclosed solution tends to expand the membrane out into the pores of the cell thus stretching the particles of the membrane and so making ruptures more likely to occur.

The new cells are about the same size as the old, but having the membrane on the outer surface greatly increases its area, hence equilibrium is much more readily established.

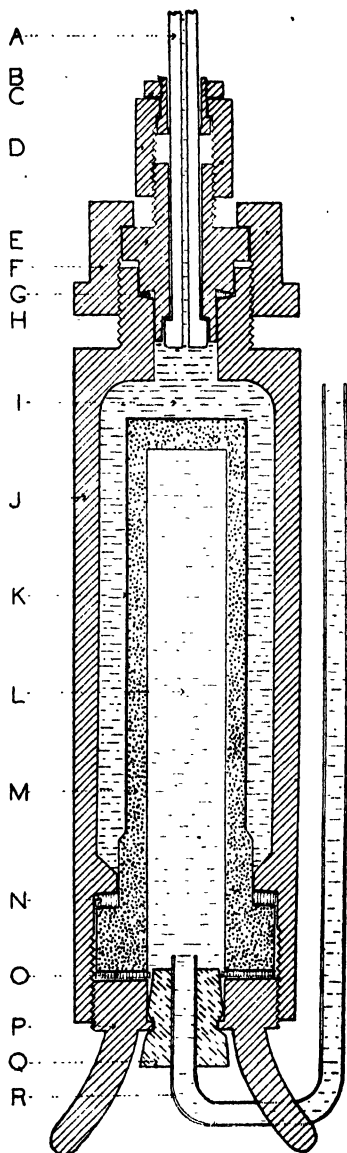


Fig. 1.

A distinct advantage in construction is apparent in the method of attaching the manometer. In the case of the old apparatus the lower end of the manometer terminated in a rubber-covered, cone-shaped attachment which was forced into the tapered neck of the cell. This often resulted in splitting the cell simply by the mechanical pressure used in securing a tight joint between manometer and cell. In the apparatus described above it will be noticed that the manometer is attached, not to the *cell*, but to the bronze cup, hence a tight joint is easily secured without danger of breaking the cell.

This form of apparatus fulfilled all expectations, proving convenient, strong, and of quick action, as the results of Experiments No. 1 to 7, inclusive (see data which follows) show. Equilibrium was reached in from 10 to 12 hours and in even less time when the initial pressure was as much as half the equilibrium pressure. The so-called "Thermometer effects,"<sup>1</sup> which were so troublesome with the old type apparatus, proved negligible in the new form of cell. Solutions whose osmotic pressures are not over 100 atmospheres can be measured with ease and expediency in the apparatus as described. It was impossible, however, to get glass manometers which would withstand greater pressure than this. Experiment No. 5 was the only successful measurement of a higher pressure (124 atmospheres) and this could not be duplicated. In Experiment No. 7 a pressure of 165 atmospheres was recorded for a few hours before the manometer broke. Having strengthened the cell successfully, the problem resolved itself into a matter of securing a suitable means of measuring the higher pressures with a fair degree of accuracy.

The solution of this question was found in the electrical resistance<sup>2</sup> gage, the form adopted being that developed and used by Johnston and Adams in their work on high pressures at the Geophysical Laboratory, Carnegie Institution, Washington. They kindly lent one of their gages for this preliminary test of the method, and gave detailed instructions for the construction, calibration and use of this type of gage. The principle upon which this method of measuring pressure is based, is that the resistance of certain conductors to an electric current increases with pressure, the relation being very nearly linear. Pressures are measured by comparing the resistance of two similar resistance coils when both are subjected to the *same* pressure (that of the atmosphere), and again when one is subjected to the pressure to be determined. The change in resistance which the gage coil undergoes is a measure of the magnitude of the pressure in question.

The coils used in this instance were each made from 1 meter of No.

<sup>1</sup> *Pub. Carnegie Inst.*, No. 198.

<sup>2</sup> Lisell, Dissertation, Upsala, 1903; Lafay, *Compt. rend.*, 149, 566-569 (1909); Bridgman, *Proc. Am. Acad. Arts & Sci.*, 47, 11, 335 (1911); 49, 11, 640 (1913).

40 "Therlo" wire, double silk covered, wound noninductively upon a mica frame. This frame was made of two plates of mica intersecting each other at right angles. The coils were shellaced, baked, temperature seasoned at 150° for 16 hours, pressure seasoned at 1000 atmospheres for 24 hours, and at 8000 atmospheres for one-half hour. All joints to terminals and leads are silver soldered, to insure constancy of resistance.

"Therlo" is an alloy of copper, manganese and aluminium, and is used on account of its low temperature coefficient (+0.000056 per degree centigrade) and its negligible thermoelectric effect against copper. Compared with manganin, these factors are considerably smaller and the therlo has the further advantage of being more stable in its electrical and mechanical behavior. Its specific resistance is also higher than that of manganin.

The pressure coefficient of resistance for therlo is slightly more than two parts per million per atmosphere, the exact value depending upon the previous history.

The coils as made above have a resistance of about 100 ohms. Hence, in order to measure pressures accurately to  $\frac{1}{10}$  of an atmosphere it is necessary to have a means of measuring changes in resistance of one part in five million. This requirement is met in the Leeds and Northrup Carey Foster Bridge used with their new high sensitivity galvanometer. This outfit, when used with the 100 ohms coil above, has a sensitivity of 0.00001 ohm over a range of 0.01 ohm change in resistance, corresponding to a pressure range of 50 atmospheres; and a sensitivity of 0.0001 ohm over a range of 0.1 ohm change in resistance, corresponding to a pressure range of 500 atmospheres. The latter combination is the one used in this work,—however a plan is in mind for securing the greater sensitivity over the greater range and will be tried when such refinement seems justified.

The courtesy of the Geophysical Laboratory was extended to the authors who took advantage of the opportunity to calibrate this secondary gage against an absolute gage, in terms of resistance as measured by the Carey Foster Bridge. The calibration data follow in Table I.

TABLE I.

Pressure on absolute gage (atmos.).	Change in resistance of gage coil (ohms $\times 10^4$ ).			Change in resistance per atmos. (ohms $\times 10^4$ ).	Deviation from a change in resistance $2 \times 10^{-4}$ ohms per atmos. (ohms $\times 10^4$ ).
	No. 1.	No. 2.	Mean.		
17.9	37.0	36.95	37	2.0670	—1.2
83.3	172.0	172.0	172.00	2.0648	—5.4
148.5	308.9	308.1	308.50	2.0774	—11.5
213.8	445.8	446.1	445.95	2.0858	—18.35
279.1	582.7	583.1	582.90	2.0885	—24.7
344.4	721.3	719.8	720.55	2.0922	—31.7
409.8	860.3	856.1	858.40	2.0949	—38.8
Additional value on last point	858.8				

For a working calibration curve the deviations given in the last column were plotted against the mean changes in resistance.

The details of construction of the gage as adapted for use in this work are shown in Fig. 2. Z is the coil described above, the terminals of which are hard soldered to the copper lead wires U and U'.

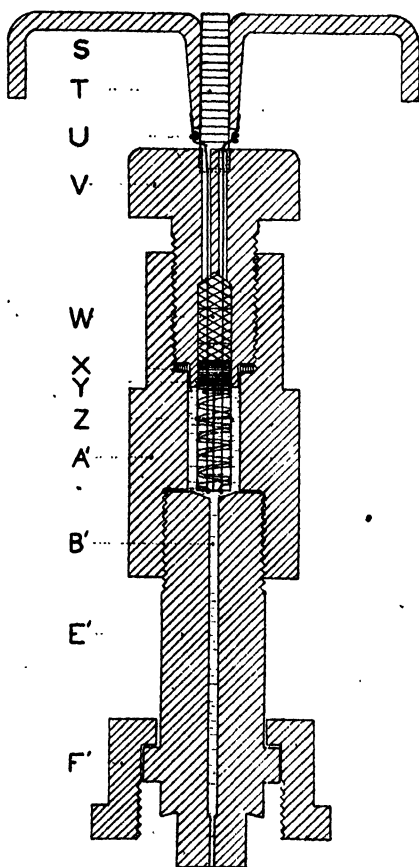


Fig. 2.

which the lead wires pass to the exterior and which screws into A' against the copper washer X. W and Y are packing to prevent leaks around the lead wires. W is composed of three layers of soapstone (alberine) carefully cut and drilled to fit the opening in V and the wires U and U'.

These soapstone plugs were forced into place by application of sufficient mechanical pressure to crush the stone and compress it securely in V tight around the wires. A knot was made in the wires between two of the layers of stone to prevent subsequent flowing of the copper under pressure. The exposed layer of stone was coated with marine glue and after drying a layer of molten Khotinsky wax (Y) was poured on. The function of the latter is chiefly to prevent movement of the lead wires, which causes a loosening of the soapstone around them. Some trouble with leakage on this account was experienced at first, but with the present arrangement there is none. The lead wires at the exterior end are hard-soldered to

heavy copper terminals S and S', which were amalgamated and dip into the mercury cups of the Carey Foster Bridge coil holder.

E' is the attachment by which the gage is connected to the osmotic pressure apparatus. The parts E' and F' in Fig. 2 correspond to parts E and F in Fig. 1 and serve as a means of connecting the resistance gage and the glass manometers respectively to the bronze cylinder J (Fig. 1). The coil Z is immersed in oil which fills the compartments in A' and E' as indicated by B'. The solution I (Fig. 1) is in contact with the oil at the lower end of the capillary opening in E' (Fig. 2). The compression



of the oil allows some of the solution to be forced up into this capillary. This necessitates frequent renewal of the oil. A mercury trap at the lower end of E' would obviate this difficulty. The comparison coil is immersed in oil in a brass cup and connected by means of mercury contacts to the other arm of the Carey Foster Bridge coil holder.

This gage presents many very decided advantages over the manometric method of measuring pressures. The strength is well nigh unlimited. The old type manometers, depending as they do upon the compression of a gas, involve a considerable change in volume. The only change in volume suffered in the resistance gage is that due to the compression of the oil. Hence dilution of the solution being measured is reduced to a minimum, and as a result, equilibrium is much more rapidly established. Furthermore the deviations of gases from Boyle's law make the manometric method less accurate at high pressures. The percentage error involved in reading the levels of the mercury menisci also increases with the compression of the gas to a small volume. So the higher the pressure the less sensitive the manometer becomes. On the other hand, the sensitivity of the resistance gage does not decrease with the pressure.

The results obtained with the modified osmotic pressure cell equipped with the resistance gage are most gratifying. Equilibrium is reached in from an hour and a half to six hours, depending upon the concentration of the solution and the initial pressure developed by compression of the rubber washers. This makes it possible to secure a satisfactory measurement within 24 hours. In this connection especial attention is called to Experiments Nos. 12, 18, 19, 20 and 22.

The objection raised by certain critics of the Morse and Frazer method, on the grounds that the solution is not stirred, may be legitimate in the case of these more concentrated solutions when measurements are completed in such a short time. The solutions are very viscous but the amount of water transferred into the solution is small and the area of the membrane is large. Hence it is but a thin film of water over the surface of the cell which must diffuse through the solution. As to whether or not stirring is essential can only be proven by trial. It is planned to introduce a stirring device into this form of apparatus in the near future and settle the question. Such an arrangement may at least hasten the establishment of equilibrium, although the speed with which equilibrium is apparently reached in the present apparatus leaves but little to be desired.

### Experimental.

**Preparation and Analysis of Solutions.**—This work was all done at 30° the apparatus, including the Carey Foster Bridge, being kept in a carefully regulated thermostat.

Aqueous solutions of cane sugar were studied over the complete range

of solubility. The sucrose used was carefully purified from rock candy. To facilitate ready comparison with previous work done in this laboratory, the solutions were all made up on the weight molar basis using atomic weights on the  $H = 1$  scale. The concentrations are expressed also in terms of  $O = 16$ . The sugar in each instance was dissolved in conductivity water made 0.01 ion normal with potassium ferrocyanide. The solvent against which the osmotic pressures were measured was 0.01 ion normal copper sulfate. The presence of the "membrane formers" repairs ruptures in the membrane made by the pressure. The specific gravity was determined for each solution; so that concentrations might also be expressed in terms of the volume molar system. This was for the purpose of comparison with measurements made by Berkley and Hartley and others who expressed the concentrations in terms of the volume molar system.

The extent to which the solutions were diluted during measurement was ascertained by the saccharimeter in the following manner:

From the optical rotation, the concentration was determined by reference to a curve made by plotting the values of the ratios of the concentrations of the original solutions to their optical rotations against *their* optical rotations, *i. e.*, letting  $C$  represent the concentration, and  $r$  the optical rotation, the values of  $C/r$  were plotted against the values of  $r$ . By multiplying the optical rotation of a given solution by the corresponding value of  $C/r$  as determined from the curve, the concentration of the solution in grams of sugar per 1000 g. of water was obtained.

In the work on dilute solutions carried on in this laboratory, corrections for changes in concentrations are made by changing the observed pressure the same per cent. that the optical rotation of the solution changes during the measurement. This involves two errors, for it assumes that the change in optical rotation is linearly proportional to the change in concentration and that the osmotic pressure is a linear function of the concentration. The magnitude of the error may be negligible in the case of dilute solutions but in the case of concentrated ones the error would be enormous. Hence in this work the final concentrations are determined from the curve described above and the observed osmotic pressures are recorded as the pressures of solutions of these concentrations.

The contents of the solvent compartment (L, Fig. 1) were examined after each experiment to determine to what extent the sugar had leaked through the membrane.

The amount of sugar in the "solvent" could not be detected by the saccharimeter in the case of experiments measuring pressures of solutions up to 5M concentration. In the experiments with the more concentrated solutions (5M and above), the solvent showed an optical rotation of  $0.5^\circ$ , which corresponds to an error in the measurement of the pressure of not more than 0.1 atmosphere and this is within the limits of accuracy

of the method at these pressures (150 to 250 atm.). In Experiments No. 16, No. 18 and No. 23, the leakage was somewhat more, due no doubt to the unseasoned conditions of the cells, as mentioned below. The results of these experiments are not considered of value.

### Results.

Table II gives a somewhat detailed account of representative experiments. From this can be seen the speed with which measurements can be obtained. Experiment No. 3 was made with a glass manometer, the others with the resistance gage.

In this table  $R$  is the resistance in ohms of the membrane.  $C$  is the original concentration of the solution expressed in weight molar terms ( $H = 1$ ).  $\alpha$  is the optical rotation of the solution after the experiment and  $c$  is its final concentration, expressed in grams of sugar per 1000 g. of water.  $t$  is the time that the reading was made, expressed in hours after the time at which the cell was set up.  $\Delta R$  is the change in resistance of the gage coil expressed in ten thousandths of an ohm (ohms  $\times 10^4$ ).  $P$  is the observed osmotic pressure.

TABLE II.

Experiment No. 3. Cell No. 6; $R$ 13,400. $C = 3M$ ; $\alpha = 227.4^\circ$ ; $c = 957.354$ .		Experiment No. 12. Cell No. 5; $R$ 31,000. $C = 4M$ ; $\alpha = 273.6^\circ$ ; $c = 1300.97$ .	
Time (hours). $t$ .	Pressure (atmos.). $P$ .	Time (hours). $t$ .	Pressure (atmos.). $P$ .
19	87.28	0.1	80.0
26	88.05	1.0	129.3
45	88.21	3.0	131.1
66	88.21	4.0	131.3
90	88.56	5.25	131.4
114	88.21	5.75	131.5
128	88.06	Equilibrium pressure 131.5	
152	87.82		
176	87.68		
Equilibrium pressure	88.10		
Experiment No. 20. Cell No. 4; $R$ 25,000. $C = 3M$ ; $\alpha = 234.8^\circ$ ; $c = 1007.21$ .		Experiment No. 22. Cell No. 5; $R$ 44,000. $C = 5M$ ; $\alpha = 306.0^\circ$ ; $c = 1618.74$ .	
Time (hours). $t$ .	Pressure (atmos.). $P$ .	Time (hours). $t$ .	Pressure (atmos.). $P$ .
0.5	79.0	0.1	85.6
1.5	93.9	1.0	165.7
2.5	94.7	3.0	175.8
4.5	93.7	4.0	175.7
6.0	93.9	5.0	175.8
7.5	94.2	10.0	176.1
17.00	94.5	21.0	175.3
19.00	94.3	22.0	176.1
20.00	94.1	24.0	175.7
Equilibrium pressure	94.2	Equilibrium pressure	175.8

TABLE III.

Expt. No.	Grams sugar 1000 g. water.	Grams sugar 100 g. sol.	Grams sugar 1000 cc. sol.	Final conc. gms. sugar 1000 gms. water.	Time at which equilibrium was reached.	Osmotic press. in atmospheres. P.	Ratio P/ε.
1	....	....	....	33.96	3-15 days	2.474	0.0728
1	339.6	25.351	280.1700	339.60	3-15 days	27.22	0.08015
1	679.2	40.448	475.3007	676.96	29 hours	57.70	0.08524
2	679.2	40.448	475.3007	668.86	1 hour	57.47	0.08593
6	679.2	40.448	475.3007	664.98	18 hours	57.16	0.08595
3	1018.8	50.464	619.5412	957.35	19 hours	88.10	0.0920
4	1018.8	50.464	619.5412	997.24	20 hours	90.04	0.0903
19	1018.8	50.464	619.5412	1018.80	5 hours	94.75	0.0930
20	1018.8	50.464	619.5412	1007.29	1½ hours	94.20	0.0935
(5)	1358.4	57.598	730.2576	1276.76	6 hours	124.20	0.0980
8	1358.4	57.598	730.2576	1302.34	37 hours	130.80	0.1005
9	1358.4	57.598	730.2576	1289.30	6 hours	130.20	0.10098
10	1358.4	57.598	730.2576	1326.70	3½ hours	134.00	0.1010
11	1358.4	57.598	730.2576	1327.68	6½ hours	133.90	0.1008
12	1358.4	57.598	730.2576	1300.97	3 hours	131.50	0.1010
(7)	1698.0	62.932	817.7248	?	19 hours	165.00	?
(13)	1698.0	62.932	817.7248	1623.90	7½ hours	171.80	0.1058
(14)	1698.0	62.932	817.7248	1602.67	9 hours	167.60	0.1045
15	1698.0	62.932	817.7248	1597.00	16 hours	174.30	0.1091
22	1698.0	62.932	817.7248	1618.74	3 hours	175.80	0.1086
(16)	2037.6	67.079	888.3145	1932.91	17 hours	208.80	0.1080
17	2037.6	67.079	888.3145	1942.56	7 hours	220.40	0.11345
(18)	2037.6	67.079	888.3145	1982.40	5 hours	217.00	0.10946
21	2037.6	67.079	888.3145	1917.65	6 hours	216.10	0.11270
(23)	Supersaturated				7 hours	268.80	?

A summary of the results of the experiments is given in Table III. This also includes data on molar and tenth molar solutions previously determined in this laboratory. The results of Experiments Nos. 5 and 7 with glass manometers are given no importance, for they were not duplicated. No. 7 not even being completed. The results of Experiments Nos. 13, 14, 16 and 18 are also given slight consideration for these were the first times that the cells used were ever subjected to such pressures. It has long been recognized that even at much lower pressures cells must be seasoned at a given pressure before they will develop the maximum osmotic pressure of a solution and give concordant results. Hence those measurements with unseasoned cells are disregarded. All other measurements are with cells more thoroughly seasoned by being set up with strong sugar solutions in the apparatus shown in Fig. 1, having A sealed off instead of sealed to a manometer.

In the last Experiment (No. 23) a supersaturated solution of cane sugar was used, in hopes of measuring the osmotic pressure of a saturated solution. The excess sugar was more than sufficient to saturate the water that would be taken up by the solution during the measurement.

<sup>1</sup> For previous work in this laboratory, see *Pub. Carnegie Inst.*, No. 198.

The pressure developed reached the maximum during the first few hours and then gradually decreased as the excess sugar in solution gradually crystallized out. Evidently equilibrium between solid and dissolved sugar was not reached during the experiment. It was impossible to get a satisfactory analysis of the solution by the saccharimeter. There was considerable leakage of sugar through the membrane so the results of the experiment are of no value save to show the greatest pressure developed.

In Fig. 3, the data in Table III are shown graphically. The curve AB was obtained by plotting the pressures ( $P$ ) against the concentrations ( $c$ ). AC is a theoretical curve in which the calculated pressures obtained from the thermodynamic formula for osmotic pressure are plotted against the concentration. These calculations neglect association of the solvent and hydration of the solute so are of no theoretical importance but simply show the extent of the deviation from ideal conditions.

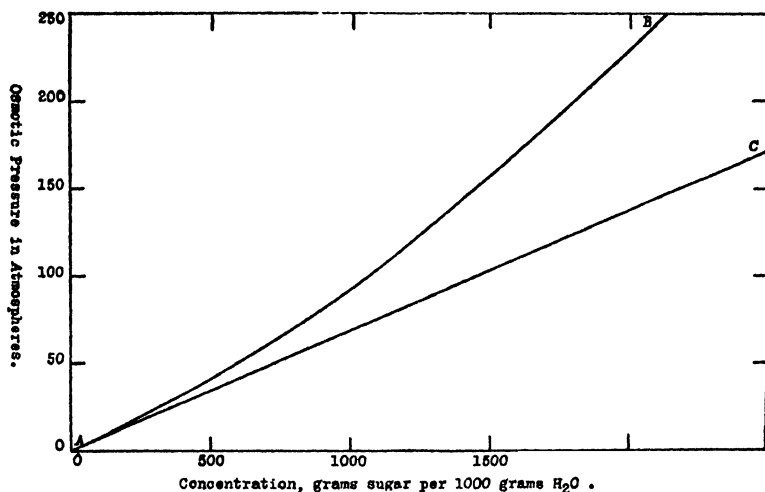


Fig. 3.

From the Curve AB, the actual osmotic pressure of a solution of sucrose of any concentration may be determined by interpolation. More exact values may be obtained from a curve made by plotting the ratio  $P/c$  (Table III) against  $c$ . The interpolated values given in Tables IV and V were obtained from such a curve.

In Table IV the results of this work are compared with the data obtained by Berkley and Hartley<sup>1</sup> in their work on cane sugar. Their measurements were made at 0° (Col. 3), the concentrations being expressed in volume molar terms (Col. 1).

<sup>1</sup> *Trans. Roy. Soc., (A)* 206, 481 (1906).

By the help of the data in Table III the concentrations were transformed to the weight molar basis and are given in Col. 2. Assuming that the temperature coefficient of osmotic pressure is the same as for gas pressure, the values at 30° given in Col. 4 were calculated from the values of Berkley and Hartley determined at zero. In Col. 5 the data obtained in this laboratory are shown, these values being determined by interpolation as explained above. The concordance is really better than might be expected.

TABLE IV.

1. Grams/1000 cc. solution.	2. Grams/ 1000 g. H <sub>2</sub> O.	3. Berkley and Hartley.		5. Frazer and Myrick. P <sub>10</sub> .
		P <sub>0</sub> .	P <sub>10</sub> = (1 + 0.00367 <i>t</i> )P <sub>0</sub> .	
180.1	202	13.95	15.48	15.59
300.2	370	26.77	29.72	29.78
420.3	569	43.97	48.81	47.88
540.4	820	67.51	74.94	73.06
660.5	1133	100.78	111.87	109.10
750.6	1430	133.74	148.46	148.80

#### Discussion.

In calculating the theoretical values of osmotic pressure it has been customary in this laboratory to use the van't Hoff equation as modified by Morse and Frazer, *viz.*:

$$P = \frac{RT}{V} n \quad (1)$$

where P is the osmotic pressure, R is the gas constant and T the absolute temperature. V represents the volume of the pure solvent in the solution at 4°, and *n* represents the number of mols of solute present. This does very well for dilute solutions, but for more concentrated solutions the more exact thermodynamic formula should be used.

As early as 1894 it was pointed out by van der Waals and his associates Boldingh and van Laar, especially the latter,<sup>1</sup> that the properties of solutions (vapor pressure, osmotic pressure, etc.) are functions not of the relation of solute particles to solvent particles, but of solute particles to the total number of particles present, or more exactly, that the properties are a function of the mol fraction of the solvent present. This view and its relation to van't Hoff's equation has also been discussed at length by many other writers, namely, Gibbs, Evans, Trevor, Lewis, and Washburn, in particular.

Van Laar's equation for the relation between osmotic pressure and concentration is

$$P = \frac{-RT}{V_0} \ln \frac{N}{N + n} \quad (2)$$

<sup>1</sup> Van Laar, *Zeit. Phys. Chem.*, 15, 457 (1894).

where  $V_o$  = the molar volume of the solvent,  $N$  = the number of mols of the solvent and  $n$  = the number of mols of the solute. If the thermodynamic relation between vapor pressure and osmotic pressure expressed by the familiar equation,

$$P = \frac{RT}{V_o} \ln \frac{p_o}{p} \quad (3)$$

is accepted, then Equation 2 follows directly from a consideration of Raoult's law.

In other words, Raoult's law states that the vapor pressure of a solution is a function of the mol fraction of the solvent present, so if there is a direct relation between vapor pressure and osmotic pressure, the latter must also be a function of the mol fraction of solvent present.

The above mentioned writers also point out that the value of Equation 1 lies in its being an approximation of Equation 2 for if  $x$  is used to represent the mol fraction of the solute present, Equation 1 may be expressed,

$$P = \frac{RT}{V_o} (x + x^2 + x^3 + \dots) \quad (4)$$

Equation 2 upon expansion becomes,

$$P = \frac{RT}{V_o} (x + \frac{1}{2}x^2 + \frac{1}{3}x^3 + \dots) \quad (5)$$

and it will be seen that the two equations differ only in the higher powers of  $x$ . If this factor is small the higher powers may be neglected and the two equations become identical.

Equation 1, as an approximation of Equation 2, gives values practically identical with those obtained from the latter in the case of dilute solutions. However, as the concentration of the solution increases, the values as calculated from the two equations differ more and more. Hence Equation 2 alone can be used correctly in the case of concentrated solutions. This has been done in all calculations in this paper.

At the pressures measured in this work the compressibility of the solution is no doubt an important factor. However, no data was available so this factor was neglected.

In the case of aqueous solutions the degree of association of the solvent must be considered as well as the hydration of the solute.

For weight normal solutions  $N = \frac{1000}{18.015.a}$  where  $a$  is the degree of association of the solvent. If we represent the degree of hydration of the solute by  $W$ , then

$$N = \frac{1000}{18.015.a} - \frac{W}{a} n$$

and the mol fraction of solvent present

$$\frac{N}{N+n} - \frac{\frac{1000}{18.015a} - \frac{W}{a} n}{\left(\frac{1000}{18.015a} - \frac{W}{a} n\right) + n}$$

The molecular volume of the solvent is equal to the volume ( $v$ ) of one gram of the solvent at the temp. ( $t$ ) multiplied by its molecular weight.

$$V_0 = v \cdot 18.015a$$

The value of  $R$  in cc. atmospheres is 82.07. Making these substitutions and introducing the factor for transference from natural to Briggsian logarithms we have as the final working form of the equation

$$P = \frac{-82.07(273.1 + t^\circ)2.303}{v \cdot 18.015a} \log \frac{\frac{1000}{18.015a} - \frac{W}{a} n}{\left(\frac{1000}{18.015a} - \frac{W}{a} n\right) + n} \quad (6)$$

No reliable data are available for the degree of association of water. However, it is the consensus of opinion<sup>1</sup> that water is a ternary mixture of mono-, di- and tri-hydrol, the di-hydrol predominating. The equilibrium, however, is greatly influenced by temperature and pressure. Increases in the former shift the equilibrium towards the mono-hydrol and increases in pressure shift the equilibrium toward the di-hydrol. So in the absence of exact figures the degree of association has been taken as 2.

Using the factors indicated in Equation 6,  $n$  must be expressed as the weight molar concentration in terms of  $O = 16$ .

Table V gives a comparison of the experimental values of osmotic pressure compared with the calculated values, assuming the various degrees of hydration indicated.

TABLE V.  
Osmotic Pressures of Cane Sugar.

Concentration. Wt. molar. H = 1.	Observed.			Calculated. Equation 6.				
			Equation 1. $a = 1.$ $w = 0.$	$a = 1.$ $w = 0.$	$a = 1.$ $w = 6.$	$a = 2.$ $w = 6.$	$a = 2.$ $w = 5.$	$a = 2.$ $w = 4.$
0.1	2.472	24.72	2.47	2.44	2.47	2.48	2.48	2.47
1	27.22	27.22	24.72	24.4	27.28	26.99	26.45	25.98
2	58.37	29.19	49.43	48.32	61.19	59.89	57.41	55.1
3	95.16	31.72	74.15	71.85	104.65	100.95	94.03	88
4	138.96	34.74	98.86	94.80	162.25	153.7	138.2	125.5
5	187.3	37.46	123.58	117.7	242.6	224.2	192.5	168.8
6	232.3	38.7	148.3	140.1	361.7	323.9	261.4	219.3
6.5	252.8	38.9	173.0	151.2	446.9	391.75	303.4	247.9

In Column 2 are found the experimental values of osmotic pressure  $P$  and in Column 3 are shown the values of "molecular pressure" at each

<sup>1</sup> Walden, *et al.*, *Trans. Far. Soc.*, 6, 71 (1910).



concentration (*i. e.*, the pressure per mol of sugar, neglecting hydration). It will be noted that these figures approach a constant value as saturation is approached.

In Columns 4 and 5 a comparison is made of the values of  $P$  as calculated by Equation 1 and by Equation 2, association and hydration both being neglected.

The curve AC in Fig. 3 is of the values in Column 5 and shows by comparison with the experimental curve AB how greatly the complications of the associations of solvent and the hydration of the sugar cause the results to deviate from ideal conditions.

Column 6 gives the values obtained when the assumption is made that a hexahydrate of constant composition is formed and that the effect of association on the results obtained is negligible. It is upon these assumptions that Washburn<sup>1</sup> bases his consideration of calculated osmotic pressures. While the concordance with the observed values is fair at lower concentrations it is obvious that the errors are considerable at higher concentrations.

Columns 7, 8 and 9 show the values obtained from Equation 6, assuming the degree of association of water as 2 and assuming the formation of the hexa-, penta- and tetrahydrates, respectively. From a consideration of Column 7 it will be seen that even when the degree of association is taken into account, the assumption that a hexahydrate is formed which is stable throughout the entire range, is unwarranted. Similarly, from Column 8, it will be seen that the assumption of Callendar,<sup>2</sup> that a stable pentahydrate exists throughout the range, is also open to objection. Both of these assumptions, however, seem to hold over limited ranges, but now that the entire range of solubility has been studied, the evidence indicates a change in the degree of hydration with changes in concentration. Up to concentrations of 2 molar, calculations based on the assumption of the formation of the hexahydrate, give results most concordant with the experimental values. At two molar concentration the experimental value is a mean between values obtained theoretically, considering the formation of hexa- and pentahydrates, respectively.

For 3 and 4 molar concentrations the assumptions of the existence of the pentahydrate gives values concordant with experimental results. At 5 and 6 molar concentrations the experimental values are intermediate between those obtained assuming the degree of hydration as five, and those assuming the hydration as four.

The extrapolated experimental value for 6.5 molar (which is practically a saturated solution) concords well with the calculated value

<sup>1</sup> "Principles of Phys. Chem.," McGraw-Hill, 1915.

<sup>2</sup> *Proc. Roy. Soc., (A)* 80, 466 (1908).

for the tetrahydrate. Hence it would seem that the degree of hydration of cane sugar in aqueous solutions decreases gradually with increase in concentration. This is in harmony with the newer hydrate theory of Jones.<sup>1</sup> Findlay,<sup>2</sup> in his discussion of osmotic pressure considers the experimental data formerly available as evidence against Jones' hydrate theory and harmonizing with the older one of Mendeleef. His conclusions, as well as those of Washburn and Callandar were simply based on considerations of too limited ranges of concentration.

### Summary.

I. In this article the authors describe a modification of the Morse and Frazer method of measuring Osmotic Pressures. The principal features of the new apparatus are: first, the reversal of the position of the semi-permeable membrane such that the pressure is developed around the outside of the porous clay cell; second, the use of an electrical resistance gage for measuring the magnitude of the pressures developed.

II. It is pointed out that this apparatus is a decided improvement over the old, and that it is much stronger and much quicker in its action. Pressures of at least 270 atmospheres can be measured and equilibrium is reached in a few hours so that measurements are completed in from 12 to 24 hours. These features make the method applicable to a study of concentrated solutions, and, it is hoped, to a study of solutions of certain electrolytes.

III. Measurements of the osmotic pressures of cane sugar solutions over the complete range of solubility are given and the results compared with those of other investigators over limited ranges.

IV. In the theoretical discussion the Morse and Frazer modification of van't Hoff's equation is compared with van Laar's thermodynamic equation, using the mol fraction basis. The necessity of using the latter in calculating the osmotic pressures of concentrated solutions is recognized by the authors, as has been done by others.

The experimental values obtained are compared with the theoretical values calculated by means of van Laar's equation, assuming various degrees of hydration of the dissolved sugar. It is pointed out that, although the theoretical calculations are based on assumptions and neglect certain factors, the evidence indicates that the hydrates of cane sugar formed in aqueous solutions are not of constant composition, as some have thought, but are of variable composition. The degree of hydration decreases with increase in the concentration of the sugar.

JOHNS HOPKINS UNIV.,  
BALTIMORE, MD.

<sup>1</sup> *Am. Chem. J.*, 33, 584 (1905).

<sup>2</sup> Alexander Findlay, "Mon. on Inorganic and Physical Chem."

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI.]

## REACTIONS IN NON-AQUEOUS SOLVENTS. I. THE ACTION OF CHROMYL CHLORIDE UPON THE PHOSPHORUS TRIHALIDES.

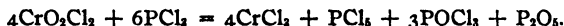
BY HARRY SHIPLEY FRY AND JOSEPH L. DONNELLY.

Received July 21, 1916.

## A. Interaction of Chromyl Chloride and Phosphorus Trichloride.

The action of chromyl chloride upon phosphorus trichloride has received very little attention. This may be due to the explosive nature of the reaction, concerning which A. Michaelis has written:<sup>1</sup>

"Chromacichlorid darf man wegen der Heftigkeit der Einwirkung nur tropfenweise zu stark abgekühlten Phosphorchlorür fließen lassen. Jeder Tropfen verursacht lebhaftes Zischen und Feuererscheinung, die jedoch nur zuerst sichtbar ist, indem sich die Retorte bald mit einem undurchsichtigen blaugrünen Anflug beschlägt. Die letzten Tropfen verursachen zuweilen Detonation. Die Reaction verlief nach der Gleichung:



"Indem aber das Phosphorsuperchlorid theilweise auf das Anhydrid einwirkte, entstand noch mehr Oxychlorid:



Since these equations have not been substantiated by quantitative data, a study of the interaction of chromyl chloride and phosphorus trichloride under new and safer conditions is of moment.

When solutions of chromyl chloride and phosphorus trichloride in *anhydrous carbon tetrachloride* are mixed there is formed at once a dark brown gelatinous precipitate which, when filtered off, washed with carbon tetrachloride and dried in a current of air free from moisture and carbon dioxide, was a finely divided gray-green powder, too deliquescent to be examined microscopically. It reacted with water (exothermic reaction) and the dark green aqueous solutions gave reaction for the following ions:  $\text{H}^+$ ,  $\text{Cl}^-$ ,  $\text{Cr}^{+++}$  and  $\text{PO}_4^{---}$ .

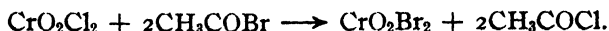
If the carbon tetrachloride solution of phosphorus trichloride is added slowly to the carbon tetrachloride solution of chromyl chloride, the volume of the precipitate increases but the color of the red chromyl chloride gradually fades to yellow and eventually becomes colorless when an excess of the phosphorus trichloride has been added. Then, of course, further additions of the trichloride yielded no more precipitate. These facts suggested the possibility of studying the reaction volumetrically provided that the end point of the reaction could be determined satisfactorily.

An accurate determination of the end point was made possible by applying a new reaction<sup>2</sup> for the detection of minute traces of chromyl

<sup>1</sup> *Jahresb. Chem.*, 1871, 248.

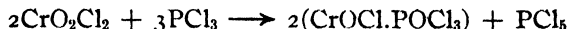
<sup>2</sup> Fry, "Notes on the Preparation of Chromyl Compounds," *THIS JOURNAL*, 33, 697 (1911).

chloride in carbon tetrachloride solution which depended upon the formation of the unstable but intensely colored *chromyl bromide* according to the equation<sup>1</sup>

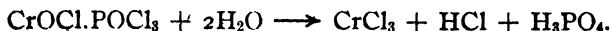


Fry found that the addition of one drop of acetyl bromide to a 0.001 molar solution of chromyl chloride in carbon tetrachloride gave an intense violet-red coloration permanent for about five minutes. Thus it is possible to titrate standard solutions of chromyl chloride and phosphorus trichloride in carbon tetrachloride to an accurate end point which is conveniently determined by removing a small drop of the reaction mixture on the end of a stirring rod and mixing it with a drop of the indicator, acetyl bromide, on a tile plate. The excessive fuming of the acetyl bromide may be modified by diluting it with carbon tetrachloride. This dilution does not interfere with the violet-red end point coloration.

In order to ascertain the molecular ratios in which chromyl chloride and phosphorus trichloride interact, 0.2 molar solutions of these compounds in carbon tetrachloride were prepared and immediately titrated from burets into 300 cc. Erlenmeyer flasks containing 100 cc. of carbon tetrachloride. An average of four titrations gave the interesting ratio in which 2 volumes of 0.2 molar  $\text{CrO}_2\text{Cl}_2$  solution were equivalent to 3.02 volumes of 0.2 molar  $\text{PCl}_3$  solution. This is practically a 2:3 ratio, i. e.,  $2\text{CrO}_2\text{Cl}_2:3\text{PCl}_3$ . The following equation, based upon this ratio, was assumed to represent the reaction in question:



The properties of the compound formed, and its analysis (described below) indicated that its composition may be represented by the formula  $\text{CrOCl}.\text{POCl}_3$ . It is decomposed by atmospheric moisture with evolution of hydrochloric acid fumes. Its decomposition by water, yielding a solution containing hydrogen-, chlorine-, chromic- and phosphate-ions, indicates that the hydrolysis may be represented by the equation



The ready and complete hydrolysis of the compound facilitated the analysis for its chromium and chlorine contents.

**Determination of Chromium.**—Weighed samples of the compound were dissolved in water.  $\text{Cr}^{+++}$  was oxidized to  $\text{CrO}_4^{--}$  by addition of sodium peroxide. Titration with standard ferrous ammonium sulfate solution gave the following results:

Substance (g.).	0.1 N ferrous soln. (cc.).	% Cr. Found.	% Cr. Theory.
0.3587	41.79	20.12	20.26
0.7109	82.70	20.14	.....

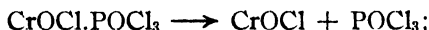
<sup>1</sup> The existence of chromyl bromide has been indicated in three other reactions, namely:  $\text{CrO}_3 + 2\text{HBr} \longrightarrow \text{CrO}_2\text{Br}_2 + \text{H}_2\text{O}$ ;  $\text{CrO}_2\text{Cl}_2 + 2\text{HBr} \longrightarrow \text{CrO}_2\text{Br}_2 + 2\text{HCl}$ ;  $(\text{HO})_2\text{CrO}_2 + 2\text{CH}_3\text{COBr} \longrightarrow \text{CrO}_2\text{Br}_2 + 2\text{CH}_3\text{COOH}$ . (Fry, *Loc. cit.*)

(The chromium was also determined by the sodium peroxide fusion method with equally concordant results.)

**Determination of Chlorine.**—Weighed samples were dissolved in water. After addition of nitric acid the chlorine was precipitated and weighed as silver chloride with the following results:

Substance (g.).	AgCl (g.).	% Cl. Found.	% Cl. Theory.
0.3938	0.8680	54.53	54.98
0.2372	0.5247	54.72	.....

Invariably, minute quantities of hydrogen chloride were lost when the compound was decomposed with water, which accounts for the slightly lower percentage of chlorine than that demanded by the theory. Nevertheless, the preceding analysis for the contents of chromium and chlorine indicate that the composition of the compound may be represented by the formula  $\text{CrOCl} \cdot \text{POCl}_3$ . Further confirmation of this formula was afforded by igniting weighed samples of the compound in porcelain crucibles, assuming that decomposition proceeded according to the equation



or to the equivalent equation



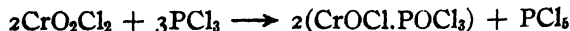
Accordingly, the residue obtained after ignition should correspond in composition to the formula  $\text{CrOCl}$  or  $\text{Cr}_2\text{O}_3 \cdot \text{CrCl}_3$ , the volatile component of the original compound being  $\text{POCl}_3$ . This is indicated by the following data:

Substance.	Residue, $\text{CrOCl}$ .	% $\text{CrOCl}$ . Found.	% $\text{CrOCl}$ . Theory.
0.3102	0.1228	39.52	40.23
0.5702	0.2252	39.48	.....

The dark green residue was insoluble in water and in concentrated acids. It was analyzed for its chromium content by the sodium peroxide fusion method with the following results:

Substance.	0.1 N ferrous soln., cc.	% Cr. Found.	% Cr. Theory.
0.2789	80.40	49.84	50.26
0.3509	100.55	49.78	.....

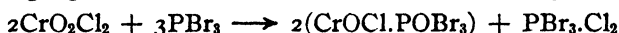
The amount of the residue left upon ignition and the percentage of chromium in the residue indicates that the insoluble product of the interaction of chromyl chloride and phosphorus trichloride in carbon tetrachloride solution may be represented by the formula  $\text{CrOCl} \cdot \text{POCl}_3$ . Furthermore, the reaction for its formation has been shown to involve 2 molecules of  $\text{CrO}_2\text{Cl}_2$  to 3 molecules of  $\text{PCl}_3$ . Hence the equation for the reaction



is warranted by the quantitative study herewith presented in Part A.

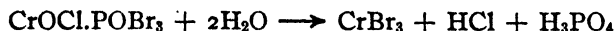
## B. Interaction of Chromyl Chloride and Phosphorus Tribromide.

Nothing was found in the literature relative to the interaction of chromyl chloride and phosphorus tribromide. When minute quantities of the pure substances are brought together the reaction takes place with explosive violence. Therefore, it is desirable to modify the reaction by dissolving the chromyl chloride and the phosphorus tribromide in anhydrous carbon tetrachloride, and to study quantitatively the interaction in the same way that the interaction of chromyl chloride and phosphorus trichloride was investigated in the preceding Part A. Here also, upon titration, one-fifth molar solutions of chromyl chloride and the phosphorus trihalide were found to interact completely in the ratio of two volumes of the former to three volumes of the latter, *i. e.*,  $2\text{CrO}_2\text{Cl}_2 : 3\text{PBr}_3$ . The end point of the reaction was readily determined by the formation of *chromyl bromide* using acetyl bromide as the indicator reagent on the porcelain tile as previously described. On the basis of the above ratio (2 : 3) the following equation was assumed for the reaction in question:



This equation is perfectly analogous to the equation for the interaction of  $\text{CrO}_2\text{Cl}_2$  and  $\text{PCl}_3$  in Part A.

The product of the interaction (presumably  $\text{CrOCl}.\text{POBr}_3$ ) after being filtered, washed repeatedly with carbon tetrachloride and dried in a current of air free from moisture and carbon dioxide, was a finely divided purple-gray powder. Its extremely deliquescent properties made it difficult to handle and prevented, with the resources at hand, a much desired microscopic examination. Its exothermic decomposition with water proceeded vigorously and the resulting green solution gave reactions for hydrogen-, chlorine-, bromine-, chromic- and phosphate-ions. Accordingly the hydrolysis may be represented by the following equation:



The solubility of the products of hydrolysis of the compound in question ( $\text{CrOCl}.\text{POBr}_3$ ) facilitated its analysis (according to methods described in Part A) for the chromium and halogen contents. The data for the chromium determinations are as follows:

Substance (g.).	0.1 N ferrous soln. (cc.).	% Cr. Found.	% Cr. Theory.
0.2310	18.45	13.83	13.34
0.3167	25.15	13.75	.....

The determination of the halogens in the compound involved the simultaneous precipitation of silver bromide and silver chloride in the molecular ratio  $3\text{AgBr} : \text{AgCl}$ . This is the ratio demanded by the assumed formula of the compound and by the equation for its hydrolysis. The assumption and formula are verified by the following analysis:

Substance (g.).	Found $\text{AgCl}3\text{AgBr}$ (g.).	Theory $\text{AgCl}3\text{AgBr}$ (g.).
0.5607	1.0238	1.0122

The results of the chromium and halogen determinations indicate that the composition of the compound may be represented by the formula  $\text{CrOCl} \cdot \text{POBr}_3$ , but its behavior upon ignition was not altogether similar to that of the preceding compound,  $\text{CrOCl} \cdot \text{POCl}_3$ , which yielded a residue corresponding in composition to the formula  $\text{CrOCl}$  or its equivalent  $\text{Cr}_2\text{O}_3 \cdot \text{CrCl}_3$ . The compound now in question,  $\text{CrOCl} \cdot \text{POBr}_3$ , yielded on ignition a purple residue which corresponded in quantity to a compound of the formula  $\text{CrOBr}$  or its equivalent,  $\text{Cr}_2\text{O}_3 \cdot \text{CrBr}_3$ , as shown by the following data:

Substance (g.).	Residue (g.).	% CrOBr. Found.	% CrOBr. Theory.
0.5002	0.1878	37.55	37.90
0.4546	0.1708	37.57	.....

This purple residue, insoluble in water and in concentrated acids, was analyzed for its chromium content by the sodium peroxide fusion method. The results of this analysis also indicate that the composition of the residue may be represented by the formula  $\text{CrOBr}$  or  $\text{Cr}_2\text{O}_3 \cdot \text{CrBr}_3$ .

Substance (g.).	0.1 N ferrous soln. (cc.).	% Cr. Found.	% Cr. Theory.
0.2076	42.25	35.37	35.16
0.2542	52.05	35.40	.....

Therefore, in conformity with the preceding analyses, the decomposition of the compound upon ignition may be represented by the equation



In conclusion, it may be noted that the reactions for the formation and the reactions for the decomposition of the compounds  $\text{CrOCl} \cdot \text{POCl}_3$  and  $\text{CrOCl} \cdot \text{POBr}_3$  are analogous.

### Summary.

1. The dangerously explosive interaction between chromyl chloride and the phosphorus trihalides can be controlled and investigated quantitatively by conducting the reactions in the anhydrous solvent carbon tetrachloride.

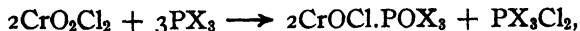
2. Equimolar solutions (0.2 molar) of chromyl chloride and phosphorus trihalide were found to interact in the ratio of two volumes of the former to three volumes of the latter, *i. e.*,  $2\text{CrO}_2\text{Cl}_2 : 3\text{PX}_3$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ).

3. The determination of this ratio by volumetric methods was rendered possible through the use of acetyl bromide as an indicator for the detection of minute traces of chromyl chloride, the end point of the reaction depending upon the formation of the unstable but intensely colored (violet-red) *chromyl bromide*.<sup>1</sup>

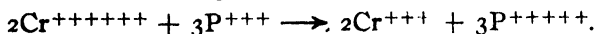
4. The new compounds thus prepared correspond in composition to the formulas  $\text{CrOCl} \cdot \text{POCl}_3$  and  $\text{CrOCl} \cdot \text{POBr}_3$ . They yielded on ignition compounds corresponding to the formulas  $\text{CrOCl}$  (or  $\text{Cr}_2\text{O}_3 \cdot \text{CrCl}_3$ ) and  $\text{CrOBr}$  (or  $\text{Cr}_2\text{O}_3 \cdot \text{CrBr}_3$ ), respectively.

<sup>1</sup> Fry, *THIS JOURNAL*, 33, 697 (1911).

5. The interactions between chromyl chloride and the phosphorus trihalides are essentially oxidation-reduction processes as shown by the composition and properties of the compounds formed. The general equation for the reactions, namely,



indicates reduction of the hexavalent chromium compound to trivalent chromic compounds and the oxidation of trivalent phosphorus halides to pentavalent phosphorus compounds. Thus, on the basis of the established 2 : 3 ratio, the above equation reduced to its simplest term becomes



CINCINNATI, O.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TEXAS.]

## THE INFLUENCE OF THE POTASSIUM ION AND OF THE CALCIUM ION UPON THE FERRI-FERRO-CYANIDE POTENTIAL.

BY EUGENE P. SCHOCH AND WILLIAM A. FELSING.

Received February 2, 1916.

OUTLINE.—1. Review of Previous Investigations. 2. Outline of Work Done and Results Attained. 3. Experimental Details and Calculation of Results. 4. Theoretical Considerations: (a) Significant Values of  $n$  and  $k$  for Ferricyanides and Ferrocyanides. (b) The Relation between the Activities and the Concentrations of the Ferricyanides and Ferrocyanides. 5. Summary.

### Review of Previous Investigations.

The earliest measurements of the potential of the ferri-ferrocyanide<sup>1</sup> electrode were made by Schaum<sup>2</sup> and showed a dependence of the potential upon the concentration represented by Peters' modification of the Nernst formula

$$E_{\text{obs.}} = E_k + 0.0002 T \log \frac{[\text{total ferricyanide}]}{[\text{total ferrocyanide}]}$$

A little later (1902) Fredenhagen<sup>3</sup> obtained the same result.

However, the result announced by these investigators is not true in general but it is only true for a series of solutions in which the total ion concentration is constant. This was shown conclusively by Lewis and Sargent,<sup>4</sup> who made a rigorous test of the rule of mixtures by making up mixtures with constant potassium ion concentrations, but different ferri-ferrocyanide concentrations, and measuring their potentials. These

<sup>1</sup> The term "ferri-ferrocyanide" is used in this paper to denote any mixture containing both potassium (or calcium) ferricyanide and potassium (or calcium) ferrocyanide with or without the chloride of the same metal.

<sup>2</sup> *Z. Elektrochem.*, 5, 316 (1899); see also *Ibid.*, 9, 406 (1903).

<sup>3</sup> *Z. anorg. Chem.*, 29, 398 (1902).

<sup>4</sup> *THIS JOURNAL*, 31, 355 (1909).



solutions were made by adding very small amounts of ferrocyanide and ferricyanide to solutions with relatively high concentrations of potassium chloride. The authors found that, as long as the  $K^+$  ion concentration was kept constant, variations of the potential obtained by varying the ratio of the ferrocyanide to the ferricyanide concentration agreed to 0.1 millivolt with the differences calculated with the Nernst-Peters formula above.

Lewis and Sargent showed also that variations in  $K^+$  ion concentration affect the ferri-ferrocyanide potentials very extensively, an increase in potassium ion concentration making the potential more positive. The amount of this change is much greater than the change of potential calculated from the change in the ratio of the concentrations of free ferricyanide to free ferrocyanide ions if the latter are calculated from conductivity ratios.

E. Mueller<sup>1</sup> has shown recently that the influence of the potassium ion upon the potential of mixtures with high concentrations of potassium ion is expressed by the following formula:

$$E_{\text{obs.}} = E_k + 0.0002 T \log \frac{[\text{total ferri.}] \times [K^+]}{[\text{total ferro.}]}$$

This relation Mueller found to be true for ferro-ferricyanide solutions which are from 0.2 to 1.0 *N* with respect to potassium chloride, but it is not true for more dilute solutions.

The foregoing presents the latest work upon the subject of this paper which has come to our notice.

### Outline of Work Done and Results Attained.

In order to gain farther insight into the concentration relations in ferri-ferrocyanide mixtures, we prepared two series of mixtures and measured their specific conductivities, and their potentials against a standard electrode. In one series, the mixtures contained only potassium ferricyanide and potassium ferrocyanide, while in the other series the mixtures contained potassium chloride in addition to these salts. The concentrations of the two or three salts in the mixtures are given in Table II at the end of the next section of this paper. Both series begin with very dilute mixtures, and extend to moderately concentrated mixtures, and the relative proportions of the two or three salts are varied extensively. The experimental details of this work are presented in the next section of this paper, and the results of the measurements are given in Table II.

The calculation of the concentrations of the ions and of the un-ionized molecules in these mixtures was made under the assumption that intermediate ions are not formed, and that the degrees of ionization are given

<sup>1</sup> *Z. physik. Chem.*, **88**, 46 (1914).

by the conductivity ratios of the salts. But before this could be done, it was necessary to determine the conductivity-concentration curves of potassium ferrocyanide and of potassium ferricyanide, and to obtain from these the ionic conductances of the ferrocyanide ion and of the ferricyanide ion. The values obtained for the latter were checked by the determinations from calcium ferrocyanide and calcium ferricyanide. The conductivity data for these salts are given in Table I at the end of the next section. All concentrations in this article for which the concentration units are not stated are expressed in milli-equivalents per liter!

With these conductivity data, the concentrations of the ions in the ferri-ferrocyanide mixtures were then calculated by a method which has been described by Sherrill<sup>1</sup> and others. The results of these calculations are given in Table II.

In order to determine whether or not the rule of "isohydric" mixtures holds with mixtures containing salts of the uni-trivalent and uni-quadrivalent types, the specific conductances of these mixtures were measured and compared with values calculated on the basis of these assumptions.

A comparison of the calculated with the observed conductances of these mixtures (see Table II, last two columns) reveals that for nineteen out of the twenty-eight mixtures these two values either agree very closely, or the calculated values are higher by less than 1%. In four other mixtures (Nos. 14, 17, 21, and 22) the calculated values are nearly 2% higher than the observed; and in Mixtures 9, 10, 23, 27, and 28 the calculated values are from 2 to 3% higher than the observed.

The observed conductances of Mixtures 1-8 and 13-22 inclusive are more dependable than the others because they were checked, not only with mixtures made from the same stock solutions, but also with mixtures made from different stock solutions. For ten of these eighteen mixtures, the calculated conductances exceed the observed by less than 0.5%; for four others, the calculated conductances exceed the observed by about 1%, and for the remaining four, the calculated values exceed the observed by a little less than 2%. The duplication with mixtures from different stock solutions served to eliminate several observed values which differed by more than 2% from the calculated values, and hence it is likely that similar duplication with Mixtures No. 9, 10, 23, 27, and 28 would reduce the differences between their calculated and observed conductances to less than 2%.

The agreement between the calculated and observed conductances of these mixtures is sufficiently close to justify the conclusion that the rule of mixtures holds for mixtures of salts of the uni-trivalent and uni-quadrivalent types.

<sup>1</sup> THIS JOURNAL, 32, 741 (1910).

Since the difference between the potentials of the two ferri-ferrocyanide mixtures is much larger than the potential difference calculated from these "calculated" concentrations of the ferricyanide ion and ferrocyanide ion by means of the Nernst-Peters formula

$$E_{(25^{\circ} \text{ C.})} = E_k + 0.0591 \log \frac{[\text{ferricy. ion}]}{[\text{ferroc. ion}]},$$

and since it is known that the potential also depends upon the concentration of the potassium ion, the idea naturally presented itself to introduce in this formula, under the logarithm, the concentration of the potassium ion raised to a power,  $x$ , which is to be determined by trial. Thus modified, the formula has the form,

$$E_{\text{obs. } 25^{\circ} \text{ C.}} = E_{k_1} + 0.0591 \log \frac{[\text{ferricy. ion}] \times [\text{K}^+]^x}{[\text{ferroc. ion}]} \quad (I)$$

With the concentrations of the ferrocyanide, ferricyanide, and potassium ions expressed milliformal, it was found that values of  $x$  extending from 0.725 to 0.750 gave fairly constant values for  $E_{k_1}$ . The variations in the values of  $E_{k_1}$  obtained with different values of  $x$  extending from 0.6 to 0.8 are shown in Table IV. With  $x = 0.725$  the maximum difference between individual  $E_{k_1}$  values is 4.3 millivolts; with  $x = 0.75$  it is 4.4 millivolts; while with other values of  $x$ , the maximum differences between individual  $E_{k_1}$  values are much greater.

Concerning the choice of the value of  $x$ , we observe the following: the  $E_k$  values obtained with  $x = 0.725$  or 0.750 show no progression with  $\Sigma i$  either in the series of the mixtures without potassium chloride or in the series with it; and with all kinds of mixtures the different values show equal variations on both sides of the mean. The  $E_k$  values obtained with larger or smaller values of  $x$  differ from those obtained with  $x = 0.725$  or 0.750 by the amount

$$dE_k = (0.725 \text{ or } 0.750 - x) 0.0591 \log [\text{K}^+]$$

and hence they present series of values progressing with  $\Sigma i$ . It is evident that the attempt to use  $x$  values other than 0.725 or 0.750 together with a change in  $x$  proportionate to  $\Sigma i$  and intended to eliminate the value of  $dE_k$ —that this attempt would give the same relation that a constant  $x$  would give. Hence  $x$  is considered to be constant and equal to 0.725 to 0.750.

The maximum variation of 4.3 millivolts, which the values of  $E_{k_1}$  corresponding to  $x = 0.725$  present, is not large in comparison with the total range of 152 millivolts in the potentials of the mixtures, particularly in view of the fact that the compositions of the mixtures present a range of total potassium ion concentration (or  $\Sigma i$ ) extending from 7.85 to 395 millions per liter.

In order to ascertain the nature of the causes which produce these

variations in  $E_h$ , we should note that the mixtures which contain only ferricyanide and ferrocyanide (Nos. 1 to 12, inclusive) show variations in  $E_h$  of the same extent and kind as mixtures which contain these two salts in relatively small concentrations together with potassium chloride in relatively great concentrations (Nos. 13 to 20, inclusive).

An idea of the extent to which the contact potentials in these cells may affect the observed potentials can be obtained by a comparison of some of these. Since the equivalent conductance of the ferrocyanide ion at 25° is 111 mhos, that of the ferricyanide ion 93.2 mhos, and that of the potassium ion 74.8 mhos, it follows that the contact potential between a solution containing mainly potassium ferrocyanide and the solution of potassium chloride in the calomel electrode (as in Nos. 9 and 11) will be greater than the contact potential between a solution containing mainly potassium ferricyanide—but with the potassium ion of the same concentration as in the ferrocyanide solution—and the same calomel electrode (as in Nos. 10 and 12, respectively). These contact potentials act in such a sense as to *increase* the observed potentials of the cells, because the ferri-ferrocyanide poles are positive to the calomel electrode; and in accordance with these considerations, we find that the  $E_h$  value of No. 9 is 0.7 millivolt greater than that of No. 10, while that of No. 11 is 2.1 millivolts greater than that of No. 12. Again, the contact potential between the calomel electrode and any particular one of our solutions containing mainly potassium chloride should be less than that between the same calomel electrode and any of our ferri-ferrocyanide mixtures containing no potassium chloride but with the potassium ion of the same concentration as the particular "potassium chloride" solution selected: this is shown to be the case with Nos. 8 and 18 (difference 2.7 millivolts), Nos. 4 and 15 (difference 2.9 millivolts), Nos. 5, 16, and 22 (difference 2.2 millivolts), Nos. 7 and 17 (difference 0.4 millivolt). These observations indicate the amount of variation due to the contact potential, and they also indicate that the variations in the values of  $E_h$  are due largely, if not entirely, to the contact potential. In any case, the variations not thus accounted for do not exceed 2 millivolts, and they affect the two series of mixtures—*i. e.*, with and without potassium chloride—alike.

The average value of  $E_h$ —the normal potential—obtained with  $x = 0.75$  is + 0.0526 volt. With  $x = 0.725$ ,  $E_h$  is equal to +0.0554. This is the potential of the ferro-ferricyanide electrode with all active components at unit concentrations, with this electrode measured against the "normal" calomel electrode, at 25°, and with a saturated potassium chloride solution between the two electrode liquids. Since in the general formula the expression under the logarithm contains two concentration factors in the numerator, but only one in the denominator, the numerical value obtained from the formula depends upon the units in which the

molecular concentrations are expressed. The  $E_{h_1}$  values presented in this paper are obtained by expressing concentrations in millimols per liter; hence if they were expressed in mols per liter, the  $E_{h_1}$  value would be different by an amount equal to  $0.0591 \log 1000 = 0.1773$  volt, and its value would be

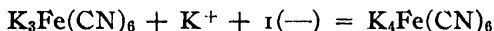
$$E_{h_1} = +0.0526 + 0.1773 = +0.2299 \text{ volt, if } x = 0.75,$$

or

$$= +0.0554 + 0.1773 = +0.2327 \text{ volt, if } x = 0.725.$$

It should also be noted that this  $E_{h_1}$  value is, as it should be, different from the ordinary "normal" potential which is 0.4 volt, as given by Abegg, Auerbach and Luther.<sup>1</sup> The latter value rests upon the assumption that the ferrocyanide and ferricyanide ions alone affect or determine the potential. In reality, however, Abegg, Auerbach, and Luther's value is obtained only with a certain concentration of potassium ion, and hence is really not a *normal* potential.

Since the pole reaction in these ferri-ferrocyanide mixtures may also be expressed as follows:



it was to be expected that the potential may be expressed as a function of the un-ionized ferricyanide and ferrocyanide, together with some power of the potassium ion concentration.

It was found that the formula

$$E_{\text{obs. } 25^\circ} = E_{h_2} + 0.0591 \log \frac{[K\text{-ferricy.}-U] \times [K^+]^y}{[K\text{-ferroc.}-U]} \quad (II)$$

gives fairly constant  $E_{h_2}$  values when  $y = 0.675$ .

The "mean" values, obtained with various values of " $y$ " and with the concentrations of the substances expressed "milli-formal" are presented in Table IV. The mean  $E_{h_2}$  value obtained with  $y = 0.675$  is  $+0.0753$  and the maximum difference between individual  $E_{h_2}$  values is 6 millivolts.

In order to throw further light upon the relation of the "cation" concentration upon the ferri-ferrocyanide potential, this work with the potassium salts was repeated with the corresponding calcium salts. Special experimental details concerning the preparation of these salts, etc., are given below, under a separate heading, together with other experimental details. The conductivity data for the separate calcium salts are given in Table I, and the data for the mixtures of calcium salts are given in Table III.

A glance at the last two columns in Table III reveals that the observed and the calculated specific conductivities of the mixtures of calcium salts agree fairly well with each other and thus corroborate the results obtained with the potassium salt mixtures.

<sup>1</sup> *Abh. Bunsen Ges.*, No. 5 (1911).

The potentials of the calcium salt mixtures also corroborate the results obtained with potassium salt mixtures. Thus with the formula

$$E_{\text{obs. } 25^\circ} = E_k + 0.0591 \log \frac{[\text{ferricy. ion}].[Ca^{++}]^z}{[\text{ferroc. ion}]} \quad (\text{III})$$

a fairly constant set of  $E_k$  values is obtainable. The values of  $E_k$  calculated, with various values of  $z$ , by means of the data and measurements of the mixtures of calcium salts are given in Table IV.  $E_k$  values obtained with  $z = 0.625$  have a mean value of  $E_k = 0.0916$  and a maximum difference between individual  $E_k$  values equal to 1.7 millivolts only.

The formula

$$E_{\text{obs. } 25^\circ} = E_k + 0.0591 \log \frac{[\text{Ca-ferricy.-U}].[Ca^{++}]^q}{[\text{Ca-ferroc.-U}]} \quad (\text{IV})$$

gives fairly constant  $E_k$  values with  $q = 0.575$ ; the mean  $E_k$  value is 0.1415 and the maximum difference between individual  $E_k$  values is 4.1 millivolts. Table IV shows the different values of  $E_k$  calculated by assigning different values to  $q$  in the potential Formula IV.

This completes the presentation of the results obtained directly from the experiments.

### Experimental Details and Calculations of Results.

**A. Preparation of Solutions and Determination of Conductivities.**—The details of the preparation of the different solutions and of the determinations of their conductivities are given under their respective headings in Notes 1 to 6 below, and the conductivity data are given in Table I.

*Note 1. Potassium chloride:* The values for the conductivities at  $25^\circ$  for this salt were taken from the tabulated results of Noyes and Falk<sup>1</sup> and are found in Table I. The salt which we used in our ferri-ferrocyanide mixtures was "C. P." stock recrystallized twice from conductivity water; the stock solutions were made up by carefully weighing out the required amount of the carefully dried salt and dissolving in conductivity water. The conductivity of our stock solution of potassium chloride was found to agree well with the data given by Noyes and Falk.

A Nernst conductivity vessel was used in all conductivity measurements; its capacity was determined with a freshly prepared 0.1 *N* potassium chloride solution, the specific conductance of which was taken as 0.01289 at  $25^\circ$ . The measurements were all made in a large water thermostat whose temperature remained constant at  $25^\circ$  to within  $0.1^\circ$ . Viscosity corrections were not applied to the results because we did not have accurate apparatus for this purpose.

*Note 2. Potassium ferrocyanide:* This salt was obtained pure by recrystallizing "C. P." stock twice from conductivity water. To avoid decomposition of the ferrocyanide by local overheating, hot saturated solutions were prepared by heating in a salt water bath. Stock solutions of known strength were made by accurately weighing out the carefully dried salt. Care was taken *not* to remove any of the water of crystallization of the ferrocyanide. In every case the strength of the stock solution was checked by means of titration with permanganate according to the method of de Haën.<sup>2</sup>

<sup>1</sup> THIS JOURNAL, 34, 454 (1912).

<sup>2</sup> Ann. Chem. Pharm., 90, 160 (1854).

The conductivities of these stock solutions of potassium ferrocyanide agreed well with previously published results.<sup>1</sup> The conductivity data for the higher concentrations of the potassium ferrocyanide as found in Table I were taken from measurements made in this laboratory.

*Note 3. Potassium ferricyanide:* This salt was prepared pure by recrystallizing "C. P." stock twice from conductivity water. The "standard" stock solutions were prepared by weighing out the carefully dried salts and checking the strength by reducing the ferricyanide in alkaline solution by means of ferrous sulfate to ferrocyanide, and then titrating with permanganate. The conductivities of the stock solutions prepared at various times were found to agree well with each other.

*Note 4. Calcium chloride:* The calcium chloride solutions were prepared by treating, in a calibrated volumetric flask, the required amounts of dry calcium carbonate (obtained by repeatedly washing freshly precipitated calcium carbonate) with the required amounts of hydrochloric acid of known strength. The solutions, after reaction, were boiled carefully to expel all carbon dioxide, and the solution diluted up to the mark with conductivity water. The strengths of these solutions were checked by means of the oxalate-permanganate titration and the silver chloride precipitation.

*Note 5. Calcium ferrocyanide:* This salt was prepared pure by recrystallizing "C. P." stock twice from conductivity water. The precaution for the prevention of local overheating as given in Note 2 was again observed. The salt was also prepared by treating the ether compound of hydroferrocyanic acid (in a flask with water) with an excess of purified calcium carbonate according to the method of Noyes and Johnston.<sup>2</sup> Solutions from both preparations of the salt gave the same conductivity. Stock solutions were prepared by weighing out the carefully dried salt, checking with the permanganate titration (here glacial acetic acid was used to acidify for the permanganate titration instead of sulfuric acid to avoid the formation of calcium sulfate).

*Note 6. Calcium ferricyanide:* This salt was prepared electrolytically from the purified calcium ferrocyanide. A concentrated solution of the purified calcium ferrocyanide was put into a clean porous cup and the cup placed in a glass jar containing a solution of purified potassium ferrocyanide. A platinum gauze anode and a mechanical stirrer extended into the porous cup. The cathode of platinum wire was placed into another porous cup filled with potassium ferricyanide solution in order to prevent the cathodic reduction product from reaching the anode cup. The current density employed was very low—not above 2 amperes per 100 sq. cm.—and the current was sent through the cell until a sample, tested with ferric chloride, gave no indication of ferrocyanide. The strength of the solution was determined by reducing the ferricyanide in alkaline solution by means of ferrous sulfate to ferrocyanide, and then titrating the latter with permanganate.

In order to obtain the conductivities at infinite dilution, two methods were used. In one, conductivities are plotted against concentrations and the curve extended until it cuts the conductivity axis: this point of intersection gives the conductivity at "zero" concentration. In the other—the method of Noyes and Coolidge<sup>3</sup>— $1/L$  is plotted against  $(CL)^{n-1}$ , and the value of  $n$  is taken so as to obtain a straight line: this line cuts the  $1/L$  axis at the value  $1/L_0$  ( $L_0$  being the equivalent conductivity at "zero" concentration). These two methods of determining

<sup>1</sup> THIS JOURNAL, 34, 454 (1912).

<sup>2</sup> *Ibid.*, 31, 987 (1909).

<sup>3</sup> *Pub. Carnegie Inst. Wash.*, No. 63 (1907).

$L_o$  agreed well for all the salts used in this investigation with the exception of calcium ferricyanide. For this salt, the value of  $L_o$  obtained by extending the conductivity-concentration curve until it cuts the conductivity axis is 156, while the nearest approach to this value obtainable with the second method of determining  $L_o$ —plotting  $1/L$  against  $(CL)^{n-1}$ —is 158.8. The value of  $n$  required to give this latter value of 158.8 is as high as 1.8; the value of  $n$  for potassium ferrocyanide, potassium ferricyanide, and calcium ferrocyanide which gave the *straight line*<sup>1</sup> were all the same,  $n = 1.65$ . Hence the value 156 for  $L_o$  was taken as the correct value in preference to the value 158.8.

The equivalent conductance of the ferrocyanide ion,  $L_{(\text{ferroc.})}$ , obtained from  $L_o$  of calcium ferrocyanide by subtracting the equivalent conductance of the calcium ion,  $L_{\text{Ca}}$ , from the  $L_o$  value—is 110.0, while  $L_{(\text{ferroc.})}$  obtained from the  $L_o$  of potassium ferrocyanide is 110.5— which figures agree well with each other.

The equivalent conductance of the ferricyanide ion at 25° was found to be 93.2 as determined from the potassium ferricyanide data and 96 as determined from the calcium ferricyanide data. In the calculations of the conductivities of the mixture, the value of the equivalent conductance of the ferricyanide ion was taken as 93.2, because with this value

TABLE I.  
Conductivities at 25° of the Salts Used in the Ferri-ferrocyanide Mixtures.  
(Concentrations in milliequivalents per liter.)

Conductivity of:						
Conc.	KCl.	$\text{K}_4\text{Fe}(\text{CN})_6$ .	$\text{K}_3\text{Fe}(\text{CN})_6$ .	$\text{CaCl}_2$ .	$\text{Ca}_2\text{Fe}(\text{CN})_6$ .	$\text{Ca}_3[\text{Fe}(\text{CN})_6]_2$ .
0.0	150.60	185.00	168.00	135.80	171.00	156.00
0.5	....	....	162.90	....	112.30	138.80
1.0	....	....	160.20	130.20	105.10	126.60
2.0	146.55	160.10	157.60	128.50	89.40	114.80
5.0	143.95	146.90	149.90	123.20	67.10	101.00
10.0	141.40	135.35	141.70	120.40	57.70	88.80
20.0	138.65	123.30	134.20	115.30	49.30	82.15
50.0	133.65	108.30	121.40	111.30	41.85	72.45
100.0	129.00	98.20 <sup>2</sup>	113.50	105.30	37.61	67.90
200.0	124.00	89.75 <sup>3</sup>	107.20	99.25	35.63	64.61
500.0	118.80	81.00 <sup>4</sup>	98.80	90.96	34.70	61.50
1000.0	117.40	77.20	93.60	88.08	33.86	57.74

<sup>1</sup> The  $n$  values for all these salts, determined by a method developed in this paper, are different from 1.65 and from each other; but they do not apply to solutions of very low concentrations and hence they cannot be used for extrapolation to zero concentration in order to determine the  $L_o$  values. The "straight line" extrapolation method for determining  $L_o$  was the only one available to us, and the use of  $n = 1.65$  in these  $L_o$  determinations has no connection with the use of other  $n$  values for higher concentrations.

<sup>2</sup> Repeated in this laboratory and found to agree with the data of Noyes and Falk.

<sup>3</sup> THIS JOURNAL, 34, 454 (1912).

<sup>4</sup> Concentration is 633 milliequivalents per liter.



the observed conductivities agreed fairly well with the calculated conductivities.

**B. Potential Measurements.**—The potential measurements of the different ferro-ferricyanide mixtures were made by means of an accurate potentiometer system, consisting of an extremely sensitive galvanometer of the D'Arsonval type, a Weston cell standardized by the Bureau of Standards at Washington, and a carefully prepared calomel electrode. This electrode was one of several which were found to remain constant to each other, and it was always kept in the thermostat, where all measurements were made. In the mixtures, gold electrodes are found to give more satisfactory results than platinum electrodes, which confirms the observations of Lewis<sup>1</sup> and of E. Mueller.<sup>2</sup> Since all mixtures were made up at a temperature slightly below the temperature of the bath, 25°, the

TABLE II.

Values of the Potentials and of the Specific Conductivities of the Potassium Ferri-ferricyanide Mixtures (concs. in "milliformals" per liter).

K <sub>4</sub> Fe(CN) <sub>6</sub> .	K <sub>3</sub> Fe(CN) <sub>6</sub> .	KCl.	ΣK <sup>+</sup> .	E <sub>obs.</sub>	E <sub>k</sub> calc.		Cond. obs.	Cond. calc.
					x=0.750.	x=0.725.		
1.25	1.66	None	7.85	0.1066	0.0549	0.0562	0.00138	0.00137
2.50	3.33	None	14.60	0.1173	0.0525	0.0545	0.00237	0.00235
5.00	5.00	None	23.46	0.1212	0.0546	0.0566	0.00415	0.00415
10.00	10.00	None	43.20	0.1327	0.0538	0.0564	0.00765	0.00765
12.50	16.66	None	60.40	0.1469	0.0539	0.0564	0.01058	0.01058
20.00	20.00	None	80.00	0.1442	0.0526	0.0554	0.01414	0.01414
25.00	25.00	None	97.60	0.1466	0.0511	0.0540	0.01725	0.01729
50.00	50.00	None	181.90	0.1624	0.0541	0.0574	0.03203	0.03214
90.00	10.00	None	180.75	0.1052	0.0537	0.0570	0.03354	0.03250
10.00	90.00	None	183.24	0.2176	0.0530	0.0563	0.03189	0.03115
9.00	1.00	None	24.13	0.0656	0.0549	0.0570	0.00442	0.00443
1.00	9.00	None	22.66	0.1757	0.0528	0.0558	0.00342	0.00388
5.00	5.00	5	27.58	0.1247	0.0549	0.0571	0.00478	0.00478
5.00	5.00	10	31.67	0.1252	0.0526	0.0548	0.00527	0.00537
5.00	5.00	25	43.75	0.1300	0.0509	0.0533	0.00716	0.00716
5.00	5.00	50	64.25	0.1390	0.0517	0.0546	0.01010	0.01021
5.00	5.00	100	104.55	0.1498	0.0507	0.0534	0.01593	0.01617
5.00	5.00	200	183.20	0.1597	0.0514	0.0547	0.02750	0.02785
5.00	5.00	300	248.85	0.1671	0.0531	0.0567	0.03810	0.03852
5.00	5.00	400	332.39	0.1722	0.0535	0.0564	0.05015	0.05050
10.00	10.00	10	51.22	0.1335	0.0511	0.0536	0.00868	0.00881
10.00	10.00	25	63.00	0.1386	0.0517	0.0544	0.01036	0.01057
10.00	10.00	50	83.90	0.1430	0.0507	0.0536	0.01325	0.01353
10.00	10.00	100	122.59	0.1515	0.0510	0.0542	0.01942	0.01946
10.00	10.00	250	238.30	0.1673	0.0543	0.0576	0.03603	0.03654
10.00	10.00	400	349.00	0.1725	0.0520	0.0558	0.05290	0.05290
25.00	25.00	200	250.00	0.1658	0.0529	0.0555	0.03887	0.03996
25.00	25.00	400	395.00	0.1760	0.0531	0.0568	0.06045	0.06171

<sup>1</sup> THIS JOURNAL, 31, 355 (1909).

<sup>2</sup> Z. physik. Chem., 88, 46 (1914).

potential of the mixture immediately after the preparation was slightly more positive than the final potential that it attained after 15 or 20 minutes, *i. e.*, when the mixture had attained the temperature of the bath.

TABLE III.

Values of the Potentials and of the Conductivities of the Calcium Ferro-Ferricyanide Mixtures (concs. in "milliformals" per liter).

$\text{Ca}_2\text{Fe}(\text{CN})_6$	$\text{Ca}_4[\text{Fe}(\text{CN})_6]_3$	$\text{CaCl}_2$	$\Sigma\text{Ca}^{++}$	$E_{\text{obs.}}$	$E_k (s=0.625)$	Cond. obs.	Cond. calc.
1.00	1.00	None	2.95	0.1440	0.0917	0.000777	0.000770
2.50	2.50	None	5.25	0.1554	0.0923	0.001695	0.001652
5.00	5.00	None	9.45	0.1648	0.0918	0.003066	0.002971
10.00	10.00	None	17.50	0.1744	0.0916	0.005690	0.005491
25.00	25.00	None	43.25	0.1903	0.0913	0.016850	0.013620
5.00	5.00	5	13.15	0.1698	0.0914	0.003995	0.003960
5.00	5.00	10	16.90	0.1733	0.0909	0.004945	0.004967
5.00	5.00	50	46.00	0.1879	0.0907	0.012530	0.012545
5.00	5.00	100	79.50	0.1986	0.0924	0.021430	0.021890

TABLE IV.

$E_k$  Values Corresponding to Different Values of  $x$ ,  $y$ ,  $z$ , and  $q$  in the Potential Formulas I to IV.

$$(a) E_{k_1} = E_{\text{obs.}} - 0.0591 \log \frac{[\text{ferricy. ion}]}{[\text{ferroc. ion}]} - 0.0591 (\log \Sigma i)(x).$$

Values of $x$ .....	0.65	0.70	0.725	0.75	0.775	0.80
Mean value.....	0.0640	0.0582	0.0556	0.0528	0.0499	0.0472
Max. variation.....	0.0087	0.0052	0.0043	0.0044	0.0063	0.0082

$$(b) E_{k_2} = E_{\text{obs.}} - 0.0591 \log \frac{[\text{K-ferricy.-U}]}{[\text{K-ferroc.-U}]} - 0.0591 (\log \Sigma i)(y).$$

Values of $y$ .....	0.600	0.625	0.650	0.675	0.700	0.750
Mean value.....	0.0866	0.0837	0.0817	0.0781	0.0753	0.0697
Max. variation.....	0.0095	0.0088	0.0083	0.0060	0.0082	0.0112

$$(c) E_{k_3} = E_{\text{obs.}} - 0.0591 \log \frac{[\text{ferricy. ion}]}{[\text{ferroc. ion}]} - 0.0591 (\log \Sigma i)(z).$$

Values of $z$ .....	0.600	0.625	0.650	0.675	0.700	0.750
Mean value.....	0.0934	0.0916	0.0899	0.0881	0.0860	0.0826
Max. variation.....	0.0031	0.0017	0.0031	0.0056	0.0074	0.0099

$$(d) E_{k_4} = E_{\text{obs.}} - 0.0591 \log \frac{[\text{Ca-ferricy.-U}]}{[\text{Ca-ferroc.-U}]} - 0.0591 (\log \Sigma i)(q).$$

Values of $q$ .....	0.50	0.550	0.575	0.60	0.625	0.65	0.675
Mean value.....	0.1470	0.1436	0.1415	0.1396	0.1380	0.1361	0.1343
Max. variation.....	0.0060	0.0040	0.0041	0.0049	0.0067	0.0085	0.0102

The potentials of the potassium ferro-ferricyanide mixtures did not assume a steady value after having attained the temperature of the bath: most mixtures gave potential measurements that oscillated through a range of several tenths of a millivolt. In general the oscillation amounted to about three- or four-tenths of a millivolt—a few as high as a millivolt—and different mixtures of the same composition gave practically always the same range of oscillation within the same limits. The measure-

ments\* were taken every ten minutes and the period of observation extended over two and one-half to three hours. The final potentials recorded in Tables II and III were an average of the entire series of measurements. Most mixtures were made up three times and few as many as four times. The calcium ferro-ferricyanide mixtures were extremely steady—at most, they showed much less oscillation than the potassium ferro-ferricyanide mixtures.

The numerical data and results of all this work have been presented in Tables I to IV.

### Theoretical Considerations.

(a) **Significant Values of  $n$  and  $k$  for Ferricyanides and Ferrocyanides.**—In attempting to determine the  $n$  and  $k$  values of salts, we must neglect the range of extremely small concentrations and confine our consideration to the larger concentrations, because different causes operate in the two concentration ranges to produce variations in the values of  $n$  and  $k$ . This may be seen readily from the ionization function of Kraus and Bray<sup>1</sup> for uni-univalent salts:

$$\frac{[A^+][B^-]}{[AB]} = K + k [\Sigma i]^{2-n}$$

With very small values of  $\Sigma i$ , the value of  $K$  forms a large part of the right side value, but with larger values of  $\Sigma i$ , the value of  $K$  is negligible beside the term  $k(\Sigma i)^{2-n}$ . For the latter concentration range, the Kraus-Bray equation reduces to the Storch equation

$$\frac{[A^+][B^-]}{[AB]} = k[\Sigma i]^{2-n}$$

It is evident that the application of the Storch equation to ranges of very small concentrations will require values of  $n$  which increase rapidly as  $\Sigma i$  decreases,<sup>2</sup> because this procedure amounts to neglecting the term  $K$  when its relative value is large enough to affect the result. It is evident that this cause of the  $n$  and  $k$  changes is essentially different from the cause or causes that bring about  $n$  and  $k$  changes in the ranges of higher concentrations.

If the causes of the changes in  $n$  and  $k$  which operate in the higher concentration ranges be assumed to continue *unimpaired* into very small concentration ranges, the values of  $n$  and  $k$  would tend toward certain final maximum values which we may obtain by extrapolation and which will be referred to in this paper as the  $n$  and  $k$  values at "zero concentration."

It should be noted that the formula

$$\frac{[C_i]^n}{[C_\infty]} = k,$$

<sup>1</sup> Kraus and Bray, *THIS JOURNAL*, 35, 1315 (1913).

<sup>2</sup> Bates, *Ibid.*, 35, 519 (1913).

shows that a lower value of either  $n$  or  $k$  will give a lower value for the other, even when all other quantities remain the same. Since the published values<sup>1</sup> of  $n$  for different concentration ranges correspond to different values of  $k$ , it is necessary to ascertain the nature of the change of *one* of these with concentration, while the other is kept *constant*. For this purpose, we have calculated from the data of Noyes and Falk the values of  $n$  for  $C = 200$  milliequivalents, with  $k$  from the concentration range 1-20, and have obtained the following results: the  $n$  values at  $C = 200$  thus obtained are *never greater* than those for lower concentrations, and for different salts, the "n-drops" vary considerably. Table V gives a number of values for illustration.

TABLE V.

Values of  $n$  with corresponding average values of  $k$  for certain concentration ranges;<sup>2</sup> and values of  $n$  for  $C = 200$  obtained with *maximum* value of  $k$  (from range 0.1-20) showing rate of change of  $n$  with  $\Sigma i$  (at 18°).

Salt.	Conc. range.	Corresponding $n$ and $k$		$n$ for $C = 200$ with constant $k$ .	Change of $n$ with change in $\Sigma i = 150$ .
KCl	0.1-20	1.48	47.12	1.450	0.030
	10-200	1.41	36.60		
NaCl	0.1-20	1.48	42.74	1.442	0.038
	10-200	1.41	36.00		
KNO <sub>3</sub>	0.1-20	1.53	46.33	1.519	0.011
	10-200	1.51	44.60		
NaNO <sub>3</sub>	0.1-20	1.50	42.42	1.481	0.019
	10-200	1.45	37.00		
AgNO <sub>3</sub>	0.1-20	1.53	43.83	1.526	0.024
	10-200	1.52	43.80		
K <sub>2</sub> SO <sub>4</sub>	0.1-20	1.48	19.73	1.456	0.024
	10-200	1.42	15.83		
CaCl <sub>2</sub>	0.1-20	1.43	19.72	1.402	0.028
	10-200	1.37	16.30		
MgCl <sub>2</sub>	0.1-20	1.45	20.31	1.407	0.043
	10-200	1.38	17.50		
Ca(NO <sub>3</sub> ) <sub>2</sub>	0.1-20	1.50	20.51	1.462	0.038
	10-200	1.44	18.10		
Ba(NO <sub>3</sub> ) <sub>2</sub>	0.1-20	1.53	19.58	1.527	0.003
	10-200	1.53	19.60		
Sr(NO <sub>3</sub> ) <sub>2</sub>	0.1-20	1.50	19.51	1.471	0.029
	10-200	1.46	18.20		
MgSO <sub>4</sub>	0.1-20	1.60	6.30	1.564	0.036
	10-200	1.47	4.87		
CuSO <sub>4</sub>	0.1-20	1.64	5.63	1.550	0.090
	10-200	1.47	3.80		

<sup>1</sup> THIS JOURNAL, 34, 480 (1912).

<sup>2</sup> Conductivity data from Noyes and Falk, THIS JOURNAL, 34, 454 (1912). Attention should be called to the fact that some of these  $n$  values are different from those calculated by Noyes and Falk. Our calculations were made by assuming various values for one and calculating the other with the formula  $(C_i)^n / (C_n) = k$ , and then choosing that pair of values which gave the least variation.

In order to determine the  $n$  and  $k$  for any one salt, we should take its equivalent conductivities at three slightly different concentrations, and determine the values of  $n$  which come nearest to giving straight lines—or, in other words, we should apply to them the well-known procedure of A. A. Noyes<sup>1</sup> for determining the equivalent conductivity at infinite dilution. The closer the three points are taken together, the more accurate will be the determination of  $n$  (and hence of  $k$ ); but for most salts, the changes in  $n$  and  $k$  with concentration are small enough to allow of drawing the straight line through points corresponding to a considerable range of concentrations as has been done by Noyes and Falk.<sup>2</sup>

But with ferricyanides and ferrocyanides, the  $n$  and  $k$  values vary so greatly<sup>3</sup> that the determination of the values of the latter would require the employment of three very slightly different concentrations. Instead of doing this, we made use of the following observation: it has been shown that when  $k$  is kept constant, the  $n$  values of all salts decrease with concentration; hence it follows that with  $n$  kept constant, the  $k$  values should *increase*. For those salts for which the “ $n$ -drops” (with constant  $k$ ) are small, these rises in  $k$  will be very small—and hence inappreciable over a *limited* concentration range—but for ferricyanides and ferrocyanides, the  $k$  rise should be large. Hence we calculated by means of the ionization data of our most dilute solutions of ferricyanides and ferrocyanides the  $k$  values obtained with different  $n$  values, according to the formula

$$\frac{C_i^n}{C_u} = k,$$

and then selected for each salt those  $n$  values for the “ $n$  values at zero concentration” which gave series of moderately, but plainly rising  $k$  values. The “limits” which these  $k$  values appear to approach as the concentrations approach zero were taken as the “ $k$  values at zero concentration.”

It should be realized that this relation between the changes in  $n$  and  $k$  values exists only with concentrations expressed in *whole* numbers. Since we have expressed concentrations in milliequivalents, the values used here are all greater than *one*.

In concluding this discussion of the  $n$  and  $k$  values, we present below the values for ferricyanides and ferrocyanides of the “ $n$ -drops” (with constant  $k$ ) corresponding to a  $\Sigma i$  range of 1 to 150 milliequivalents per liter. Attention should be called to the fact that all of these “ $n$ -drops” are

<sup>1</sup> *Pub. Carnegie Inst. Wash.*, 63, 50.

<sup>2</sup> *THIS JOURNAL*, 34, 480 (1912).

<sup>3</sup> It was on this account that Johnson (*THIS JOURNAL*, 31, 987 (1909)), could not obtain a straight line graph through a number of points representing a considerable concentration range.

TABLE VI.

Values of "k" for various values of "n" in the dilution formula  $\frac{[C_1]^n}{[C_2]} = k$ .

## (a)—Calcium Ferrocyanide:

Concentration.	n = 1.625.	n = 1.600.	n = 1.575.	n = 1.550.	n = 1.525.
5.0	0.998	0.983	0.965	0.946	0.932
10.0	1.102	1.069	1.038	1.008	0.977
10.0	1.232	1.171	1.121	1.072	0.922

The values obtained with the concentrations below 5.0 are irregular and hence have been omitted. The values obtained with  $n = 1.525$  show no progression with concentration; those obtained with  $n = 1.625$  show a great deal of progression; while the values obtained with  $n = 1.550$ ,  $n = 1.575$ , and  $n = 1.600$  show moderate amounts of progression, and hence these values of  $n$  have been accepted. The corresponding  $k$  values at zero concentration have been placed at 0.930, 0.945, and 0.960, respectively.

## (b)—Potassium Ferrocyanide:

Concentration.	n = 1.700.	n = 1.675.	n = 1.650.	n = 1.600.
2.0	9.430	9.335	9.130	8.920
5.0	10.180	9.850	9.510	8.910
10.0	11.000	10.340	9.950	9.030
20.0	12.320	11.520	10.800	9.520

The values obtained with the concentrations below 2.0 are irregular and are hence omitted. The values of  $n = 1.700$  show a great deal of progression; those for  $n = 1.600$  show no progression; while the values for  $n = 1.675$  and  $n = 1.650$  show a moderate amount of progression, and hence these  $n$  values have been accepted. The corresponding  $k$  value at zero concentration have been placed at:  $k = 9.0$  for  $n = 1.650$ ,  $k = 9.15$  for  $n = 1.675$ , and  $k = 9.30$  for  $n = 1.700$ .

## (c)—Calcium Ferricyanide:

Concentration.	n = 1.550.	n = 1.575.	n = 1.600.	n = 1.625.	n = 1.650.	n = 1.700.
2.0	3.34	3.36	3.40	3.43	3.46	3.52
5.0	3.52	3.63	3.74	3.85	3.97	4.21
10.0	3.49	3.58	3.80	3.01	4.08	4.52
20.0	4.06	4.31	4.56	4.85	5.16	5.87

The values obtained with the concentrations below 2.0 are irregular; the values for  $n = 1.550$  show little or no progression, while the values for  $n = 1.700$  show an excessive progression; hence the value  $n = 1.575$ ,  $n = 1.600$ ,  $n = 1.625$ , and  $n = 1.650$ , have been accepted. The corresponding  $k$  values at zero concentration have been placed at 3.30, 3.40, and 3.60, respectively.

## (d)—Potassium Ferricyanide:

Concentration.	n = 1.650.	n = 1.700.	n = 1.725.	n = 1.750.	n = 1.775.
2.0	23.18	23.96	23.35	24.70	25.10
5.0	22.05	23.75	24.63	25.53	26.60
10.0	21.75	24.25	25.62	27.00	28.45
20.0	24.15	27.65	29.10	31.90	34.20

The values obtained with the concentrations below 2.0 are irregular; the values for  $n = 1.650$  show no consistent progression, for  $n = 1.700$  not quite enough progression, while for  $n = 1.775$  the progression is excessive. The values  $n = 1.725$  and  $n = 1.750$  have been selected, and the corresponding  $k$  values at zero concentration have been placed at 22.0 and 23.0, respectively.

large, \*that the "*n*-drops" for the two potassium salts have the same value, and that those for the two calcium salts have the same value.

TABLE VII.

Rate of Change of *n* with  $\Sigma i$  and a Comparison of the (*n* - 1) Values with the Values of *x*, *y*, *z* and *q* for the Ferricyanides and Ferrocyanides of Potassium and Calcium.

Salt.	<i>k</i> value at "zero conc."	<i>n</i> value at "zero conc."	<i>n</i> values at approx. $\Sigma i = 150$ m. eq. per liter with <i>k</i> constant.	Change of <i>n</i> with change in $\Sigma i$ , 0.0—150.	<i>n</i> -1 values.	Values of <i>x</i> , <i>y</i> , <i>z</i> , and <i>q</i> .
$K_3Fe(CN)_6$ .....	22.00	1.725	C = 250 $\Sigma i = 156$	0.215	0.725	0.725
	23.00	1.750	1.510	0.233	0.750	0.750
			1.517			
$K_4Fe(CN)_6$ .....	9.00	1.650	C = 320 $\Sigma i = 149$	0.186	0.650	0.650
	9.15	1.675	1.464	0.205	0.675	0.675
	9.30	1.700	1.470	0.223	0.700	0.700
			1.473			
$Ca_3(Fe(CN)_6)_2$ .....	3.40	1.600	C = 400 $\Sigma i = 160$	0.280	0.600	0.600
	3.50	1.625	1.320	0.299	0.625	0.625
	3.60	1.650	1.326	0.320	0.650	0.650
			1.330			
$Ca_2Fe(CN)_6$ .....	0.93	1.575	C = 750 $\Sigma i = 151$	0.290	0.550	0.575
	0.94	1.600	1.260	0.310	0.575	0.600
	0.96	1.625	1.265	0.355	0.600	0.625
			1.270			

It is evident from the last two columns that

$x + 1 = n$  for potassium ferricyanide at "zero" concentration.

$y + 1 = n$  for potassium ferrocyanide at "zero" concentration.

$z + 1 = n$  for calcium ferricyanide at "zero" concentration.

$z + 1 = n$  for calcium ferrocyanide at "zero" concentration.

(b) **The Relation between the Activities and the Concentrations of the Ferricyanides and Ferrocyanides.**—For uni-univalent salts, it may be considered fairly well established<sup>1</sup> that the values of ( $2 - n$ ) are the sum of the exponents of the  $\Sigma i$  factors by which the concentrations must be multiplied or divided to obtain the activities. Thus, if  $[Tl].[Cl].[1/\Sigma i]^a$  is the product of the activities of the ions of thallous chloride, and  $[TlCl].[\Sigma i]^b$  is the activity of the un-ionized molecules, then

$$\frac{[Tl].[Cl]}{[TlCl]} = k[\Sigma i]^a + b = k[\Sigma i]^2 - n$$

If, as we assume throughout this paper, polyionic salts form no intermediate ions and that the conductivity ratio gives the percentage of salt ionized into the ordinary simple ions, then the fact that, even in mixtures<sup>2</sup> the conductivity function for polyionic salts is of the form

$$\frac{[A^{++}].[B^-]}{[AB]} = k[\Sigma i]^2 - n$$

instead of the form

<sup>1</sup> Bray, *THIS JOURNAL*, 33, 1673 (1911).

<sup>2</sup> Sherrill, *Ibid.*, 32, 741 (1910).

$$\frac{[A^{++}].[B^{-}]^2}{[AB]} = k[\Sigma i]^{3-n}.$$

This fact indicates that the relation between the concentrations and the activities of the components of polyvalent electrolytes (salts) includes another relation, different from the relation shown above for uni-univalent electrolytes, and which takes the place of—cancels—the higher powers otherwise required by the mass law. If this idea is correct, then the “cancelling” in the conductivity function for potassium ferrocyanide amounts to practically one  $[K^{+}]$  more than in the conductivity function for potassium ferricyanide. Furthermore, we have

$$\frac{[\text{ferricy. ion}].[K^{+}]^{0.750}}{[K\text{-ferricy.}-U]} = 2.3 = \frac{[\text{act. ferricy. ion}].[K^{+}]^3}{[\text{act. K-ferricy.}-U]}$$

and

$$\frac{[\text{ferrocy. ion}].[K^{+}]^{0.675}}{[K\text{-ferrocy.}-U]} = 9.15 = \frac{[\text{act. ferrocy. ion}].[K^{+}]^4}{[\text{act. K-ferrocy.}-U]}$$

Dividing *left*, *center*, and *right* of the first by the corresponding part of the last we obtain the following “concentration-activity relations from conductivities:”

$$\frac{\frac{[\text{ferricy. ion}]}{[K\text{-ferricy.}-U]}.[K^{+}]^{0.075}}{\frac{[\text{ferrocy. ion}]}{[K\text{-ferrocy.}-U]}} = 2.4 = \frac{\frac{[\text{act. ferricy. ion}]}{[\text{act. K-ferricy.}-U]}}{\frac{[\text{act. ferrocy. ion}]}{[\text{act. K-ferrocy.}-U]}. [\text{act. K}^{+}]}$$

Again, equating the expressions given by our *two* potential Formulas I and II for the potential for any particular ferri-ferrocyanide mixture, we obtain

$$E_{k_1} + 0.0591 \log \frac{[\text{ferricy. ion}].[K^{+}]^{0.750}}{[\text{ferrocy. ion}]} = E_{k_2} + 0.0591 \log \frac{[K\text{-ferricy.}-U].[K^{+}]^{0.675}}{[K\text{-ferrocy.}-U]}.$$

When numerical values are substituted for  $E_{k_1}$  (0.0526) and for  $E_{k_2}$  (0.0753), and this equation is simplified, it reduces to the *left-hand* equality in the concentration-activity relation above:

$$\frac{\frac{[\text{ferricy. ion}]}{[K\text{-ferricy.}-U]}.[K^{+}]^{0.075}}{[\text{ferrocy. ion}]} = 2.4$$

If we use activities in place of concentrations, we obtain

$$E_{k_1} + 0.0591 \log \frac{[\text{act. ferricy. ion}]}{[\text{act. ferrocy. ion}]} =$$



$$E_{h_2} + 0.0591 \log \frac{[\text{act. K-ferricy.-U}][\text{act. K}^+]}{[\text{act. K-ferrocy.-U}]},$$

and this reduces to the *right-hand* equality in the concentration-activity relation above. Hence these two equations give us the same "concentration-activity relations" as that obtained above from the conductivity functions.

This relation shows that for all values of  $\Sigma i$ —

$$x - y = n_i - n_o$$

because  $x$  and  $y$  are constant, and  $n_i$  and  $n_o$  decrease equally with  $\Sigma i$ . Since these four quantities are determined from *totally* independent data, this result shows that the "concentration-activity" relation of each component is the same in the conductivity functions as in the potential function.

It appears to us that the exponent of  $[\text{K}^+]$ —i. e.,  $x - y$  or 0.075—is the *sum* of the different powers of  $[\text{K}^+]$  which give the factors by which the different concentrations in the concentration must be multiplied to make them equal to the activities of the respective substances—as was illustrated with the thalious chloride at the beginning of this section. Seen in this light, the factor  $[\text{K}^+]^{0.750}$  under the logarithm in our potential Formula I

$$\frac{[\text{Ferricy. ion}].[\text{K}^+]^{0.750}}{[\text{ferrocy. ion}]}$$

has merely a numerical significance: it is the factor by which the concentration ratio

$$\frac{[\text{ferricy. ion}]}{[\text{ferrocy. ion}]}$$

must be multiplied to make it equal to the activity ratio

$$\frac{[\text{act. ferricy. ion}]}{[\text{act. ferrocy. ion}]},$$

and the factor  $[1/[\text{K}^+]^{0.325}]$  in our potential Formula II—

$$\frac{[\text{K-ferricy.-U}].[\text{K}^+]}{[\text{K-ferrocy.-U}]} \cdot \frac{[1]}{[\text{K}^+]^{0.325}}$$

serves the corresponding purpose. Evidently the activity of the ferrocyanide ion increases more with  $\Sigma i$  than that of the ferricyanide ion; while for the un-ionized molecules the reverse is true.

It is rather surprising that  $x$  and  $y$  are constant while the similar exponent  $n$  varies with  $\Sigma i$ . Perhaps the constancy of  $x$  is due to the chemical similarity between the ferricyanide ion and the ferrocyanide ion on account of which any "secondary" changes (with  $\Sigma i$ ) in the concentration-activity relation of one is undergone to an equal extent by the other; and since the ratio of these ions appears in the potential formula, such

secondary effects would "cancel" out. In the same way, the constancy of the other exponents  $y$ ,  $z$ , and  $q$  might be due to the chemical similarity of the other pairs of components concerned.

Finally, attention should be called to the fact that although

$$\frac{[\text{ferricy. ion}].[K^+]^{n-1}}{[K\text{-ferricy.-U}]} = k,$$

yet this relation cannot be used to substitute  $[K\text{-ferricy.-U}]$  for  $[\text{ferricy. ion}].[K^+]^z$ , because  $x$  is equal to the *maximum* value of  $n_i$  only, and not to the lower values of  $n_i$  corresponding to larger values of  $\Sigma i$ .

### Summary.

1. Conductivity measurements were made on solutions of potassium ferrocyanide and potassium ferricyanide, on solutions of mixtures of these and on mixtures of these with potassium chloride. The results were compared with results calculated by means of the rule of mixtures, and a fair degree of agreement was obtained.

2. Conductivity measurements were made on the corresponding calcium salts and on corresponding mixtures of these—with practically the same agreement between the observed and the calculated results.

3. The potentials of all these mixtures were measured against the "normal" calomel electrode.

4. The constituent ions and un-ionized molecules in all these mixtures were calculated on the assumption that intermediate ions are absent. The following empiric formulas were found to represent the dependence of the potentials upon the constituents of the mixtures through a  $K^+$  range of 10 to 400 milliequivalents per liter:

$$E_{\text{obs. } 25^\circ} = E_{h_1} + 0.0591 \log \frac{[\text{ferricy. ion}][K^+]^{0.75}}{[\text{ferrocy. ion}]}$$

and

$$E_{\text{obs. } 25^\circ} = E_{h_2} + 0.0591 \log \frac{[K\text{-ferricy.-U}][K^+]^{0.675}}{[K\text{-ferrocy.-U}]}$$

Corresponding formulas were found to hold for the calcium salts.

5. A new method was presented for deriving significant values of  $n$  and  $k$  for such salts as ferricyanides and ferrocyanides, for which these values vary greatly with the concentration. It was shown that the  $n$  values of the two potassium salts change equally with  $\Sigma i$ . The same is true for the calcium salts. It was found that the "maximum" values of  $n$  (i. e., the limits they approach with decreasing  $\Sigma i$ ) bear a simple numerical relation to the exponents of  $[K^+]$ —or of  $[Ca^{++}]$ —in the potential formulas above.

6. It was shown that certain of these observed relations are necessary consequences of the assumptions that the concentration-activity relation

of each component in the conductivity functions is the same as in the potential functions.

AUSTIN, TEXAS.

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, STANFORD UNIVERSITY.]

## THE BASIC COPPER SULFATES.

By S. W. YOUNG AND ALLEN EDWIN STEARN.<sup>1</sup>

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### Introductory.

In connection with some investigations on the genesis of copper ores, the problem of the formation and character of Brochantite or native basic copper sulfate comes under consideration. The analyses of this mineral give widely varying results, so divergent in fact as to indicate the probability that the substance is not of fixed composition. It was decided to attack the whole problem from the purely chemical side and the first results of the investigation are contained in this paper.

In looking over the literature on the basic copper sulfates one is struck at once by the large number of such compounds described. In the Gmelin-Kraut "Handbuch" some thirty-five are described as presumably definite compounds. These supposed compounds vary between the limits,  $10\text{CuO}\cdot\text{SO}_3$  and  $2\text{CuO}\cdot\text{SO}_3$ , with varying amounts of water. In some cases, salts, which differ from one another only in water content and this to only a very small degree, are given as distinct individuals. For example, one finds on record  $4\text{CuO}\cdot\text{SO}_3\cdot 3\text{H}_2\text{O}$  and  $4\text{CuO}\cdot\text{SO}_3\cdot 3\frac{1}{2}\text{H}_2\text{O}$ . Five different formulas are given for salts supposed to be identical with natural Brochantite, namely:  $4\text{CuO}\cdot\text{SO}_3\cdot 3\text{H}_2\text{O}$ ;  $7\text{CuO}\cdot 2\text{SO}_3\cdot 5\text{H}_2\text{O}$ ;  $7\text{CuO}\cdot 2\text{SO}_3\cdot 6\text{H}_2\text{O}$ ;  $3\text{CuO}\cdot\text{SO}_3\cdot 2\text{H}_2\text{O}$ ; and  $3\text{CuO}\cdot\text{SO}_3\cdot 3\text{H}_2\text{O}$ .

It seemed, on the face of it, to be highly improbable that such a large number of definite individuals of this class should exist, and good grounds for doubt are to be found by examination of the methods of preparation which have been used. Without going into detail concerning these methods, they may be fairly satisfactorily summarized under three heads:

1. Heating of copper sulfate solutions.
2. Precipitation from copper sulfate solutions by means of alkaline reagents such as sodium, potassium, calcium,<sup>2</sup> and ammonium hydroxides and carbonates, and in some cases by zinc oxide, as well as by acetates of the alkali metals.
3. Dilution of ammoniacal solutions of copper sulfate with water.

<sup>1</sup> Abstract of a thesis presented by Allen Edwin Stearn to the faculty of Stanford University, in partial fulfilment of the requirements of the degree of Master of Arts, May, 1916.

<sup>2</sup> Many salts are described by Pickering as a result of his studies of the Bordeaux mixture.

Of these methods, the second and third are open to the objections that foreign substances are present, and that the composition of the salt will naturally vary with the amount of precipitant used and presumably with the way in which it is added, whether slowly or rapidly. All three methods are open to the objection that, judging from the written accounts of the investigations, the products obtained do not represent equilibrium conditions. As will be shown in the experimental part of this paper, the reactions resulting in the formation of basic copper sulfates are extremely sluggish, requiring about three months at  $25^{\circ}$  for completion. It was with the purpose of adding something of clearness to the knowledge of these compounds that the following experiments were carried out. The general question which we set ourselves to answer is "are the basic sulfates of copper a set of compounds of definite composition, or are they a series of mixed crystals in variable proportions?"

### Experimental.

The method adopted for the production of the basic sulfates was the very simple one of allowing copper sulfate in solution in water, to combine with finely divided copper oxide. Preliminary experiments showed that this reaction was sufficiently rapid to be made use of. If copper oxide is allowed to stand at rest for three or four days in contact with a moderately strong solution of copper sulfate, it becomes thoroughly set into a hard cake of greenish gray, owing to the formation of basic salt. This cake is very hard and very difficultly soluble even in strong acids and ammonia.

Provision was made for three sets of duplicate samples, one to be run at  $25^{\circ}$ , one at  $37.5^{\circ}$  and one at  $50^{\circ}$ . In each set were six samples. These were placed in six magnesium citrate bottles, and the samples were made up as follows: In each bottle was placed 150 cc. of a solution of copper sulfate containing 0.04394 g. of copper in 1 cc. To the bottles were added amounts of copper oxide corresponding, respectively, to  $\frac{1}{4}$ ,  $\frac{1}{2}$ , 1, 2, 4 and 8 molecules for each molecule of copper sulfate. In addition to the six bottles in each set, a seventh was prepared containing one molecule of copper oxide to one of sulfate. These three extra bottles were designed to serve as check bottles from which samples might be taken from time to time in order to determine the progress and completion of the reaction. The three sets were then placed in thermostats which could be maintained to within  $0.1^{\circ}$  of the above mentioned temperatures, and were rotated continuously until equilibrium was established, as shown by samples taken from the check bottles. When the copper content of the samples of filtrate taken from the check bottles failed to show any further decrease during one week, it was considered that equilibrium had been attained. The time required for reaching equilibrium at the different temperatures is approximately shown in the following table:

Temperature.	Days required for equilibrium.
25.0°	88
37.5°	22
50.0°	15

These figures show how unreliable must be the conclusions of previous investigators, who have allowed only a few minutes, or at most a few hours (often at room temperature) for the preparation of their salts.

The treatment of the products obtained in the above manner was as follows: The bottles were taken from the thermostat one by one and the contents thrown on a rapid suction filter. As soon as filtration was complete, the solids were placed in specially prepared containers and centrifuged at high speed for an hour, after which they were air dried between watch glasses. Both filtrate and solids were preserved for analysis.

The filtrates were analyzed for copper by the electrolytic method. Through an inadvertence, they were not analyzed for sulfuric acid, as should have been done, in order to check certain conclusions based on the results of analysis of the solids. Table I gives the results of the copper determinations for all the filtrates.

TABLE I.

Amount of copper remaining in 5 cc. of the solutions. In column headed CuO are given the number of molecules of copper oxide added for each molecule of copper sulfate in the original mixtures.

CuO.	25°	37.5°.	50°.
$\frac{1}{4}$	0.1916	0.1956	0.1937
$\frac{1}{2}$	0.1606	0.1661	0.1657
1	0.1099 (0.1153)	0.1094	0.1094
2	0.0028 (0.0369)	0.0022	0.0018
4	0.0008	0.0008	0.0006
8	0.0006	0.0007	0.0002

The initial concentration was 0.2197 g. copper in 5 cc. From the table it is clear that in cases where two molecules of oxide to one of sulfate had been used the removal of copper from the solution was very nearly complete and in cases where more than this quantity of the oxide was used, the removal was always virtually complete. It is also evident that the amount of copper left in the solution is practically independent of the temperature.

In the 25° column there will be noticed two values in parentheses. These were the results obtained in the regular run of the samples. As they were markedly higher than was to be expected from the neighboring results, it was suspected that there might possibly have been formed in these cases a metastable form of higher solubility. Two new bottles were, therefore, prepared in exactly the same way as the others, except that they were seeded with a small amount of salt from some of the bottles that showed normal conduct. These were rotated for ninety days and gave the results used in the 25° column, which are in good agreement with neighboring results.

An examination of the solids obtained in the above experiments showed them to be of two sorts. Those prepared by using the smaller amounts of oxide, up to two molecules to one of sulfate, were clear light grayish green. Those containing larger amounts of oxide were darker in color and showed a tendency toward stratified settlement. This was taken as an indication of an excess of uncombined copper oxide, a conclusion which received confirmation upon a microscopic examination which showed the light green crystals of basic salt and black particles of oxide side by side. The examinations failed to yield any evidence of crystals of basic salt of more than one sort. The crystals were very minute and the evidence of the microscopic examination is of itself perhaps of but little importance, but offers some support to conclusions to be drawn later from the results of analysis.

All samples of the salts obtained, except those which showed free copper oxide, were analyzed for copper, sulfur trioxide and water. It was found that by heating to  $700^{\circ}$  for 15 hours in an electric furnace, all water and  $\text{SO}_3$  were driven off, leaving pure copper oxide showing no traces of  $\text{SO}_3$ .  $\text{SO}_3$  was determined from another sample, by dissolving in hydrochloric acid and precipitating with barium chloride. Water was determined by the difference between this result and that obtained by ignition. Copper was also determined in several samples by electrolysis and gave good checks with the values obtained by ignition. It was found to be impracticable to drive off water without also driving off some  $\text{SO}_3$ , so that direct determinations of water were not made.

In Table II there is given a summary of the analyses, averages only being given. They are the averages of at least two (and often more) determinations in every case.

TABLE II.  
Composition of the Salts.

Temp.	2 mols CuO to 1 CuSO <sub>4</sub>		1 mol CuO to 1 CuSO <sub>4</sub>		$\frac{1}{2}$ mol CuO to 1 CuSO <sub>4</sub>		$\frac{1}{4}$ mol CuO to 1 CuSO <sub>4</sub>	
50°....	CuO	66.31%	CuO	63.33%	CuO	59.69%	CuO	59.43%
	SO <sub>3</sub>	23.50	SO <sub>3</sub>	24.90	SO <sub>3</sub>	25.90	SO <sub>3</sub>	26.10
	H <sub>2</sub> O	10.15	H <sub>2</sub> O	11.80	H <sub>2</sub> O	13.80	H <sub>2</sub> O	14.00
	Total	99.96		100.03		99.39		99.53
37.5°...	CuO	66.20	CuO	63.09	CuO	59.20	CuO	58.57
	SO <sub>3</sub>	23.55	SO <sub>3</sub>	24.75	SO <sub>3</sub>	26.20	SO <sub>3</sub>	26.40
	H <sub>2</sub> O	10.15	H <sub>2</sub> O	12.30	H <sub>2</sub> O	14.55	H <sub>2</sub> O	15.10
	Total	99.90		100.14		99.95		100.17
25°....	CuO	66.31	CuO	63.21	CuO	61.15	CuO	60.82
	SO <sub>3</sub>	23.46	SO <sub>3</sub>	24.85	SO <sub>3</sub>	25.90	SO <sub>3</sub>	25.85
	H <sub>2</sub> O	10.20	H <sub>2</sub> O	12.10	H <sub>2</sub> O	13.10	H <sub>2</sub> O	13.35
	Total	99.97		100.16		100.15		100.02
25°....	CuO	66.31	CuO	64.31 <sup>1</sup>	<sup>1</sup> These analyses are from the samples whose solutions gave higher copper values than normal.			
	SO <sub>3</sub>	21.80	SO <sub>3</sub>	23.35				
	H <sub>2</sub> O	11.83	H <sub>2</sub> O	12.50				
	Total	99.94		100.16				

In Table III the results given in Table II have been recalculated so as to express the number of molecules of copper oxide and water in combination with one molecule of copper sulfate. For convenience, the amounts of copper remaining in 5 cc. of the solutions, from which the salts were formed, are also given.

TABLE III.  
Molecular Composition of Basic Sulfates.

Mols CuO to 1 CuSO <sub>4</sub> (originally).	50°.			37.5°.			25°.		
	Mols CuO to 1 CuSO <sub>4</sub> .	Mols H <sub>2</sub> O to 1 CuSO <sub>4</sub> .	G. Cu in 1 cc. sol.	Mols CuO to 1 CuSO <sub>4</sub> .	Mols H <sub>2</sub> O to 1 CuSO <sub>4</sub> .	G. Cu in 1 cc. sol.	Mols CuO to 1 CuSO <sub>4</sub> .	Mols H <sub>2</sub> O to 1 CuSO <sub>4</sub> .	G. Cu in 1 cc. sol.
2.....	1.83	1.92	0.0004	1.83	1.92	0.0004	1.84	1.93	0.0006
1.....	1.55	2.12	0.0219	1.55	2.21	0.0219	1.55	2.16	0.0220
1/2.....	1.31	2.37	0.0331	1.27	2.42	0.0332	1.38	2.26	0.0321
1/4.....	1.28	2.38	0.0387	1.23	2.54	0.0391	1.35	2.29	0.0383

### Discussion of the Results.

The first fact of importance to be noted is the negligible effect of temperature on the composition of the salts formed under otherwise like conditions. So closely do the analyses of the salts produced at the three temperatures check with one another, that it is safe to conclude that within the limits investigated the composition of the salts is independent of the temperature.

In the second place, it is to be noted that the amount of copper oxide in the salt increases with the amount added, as is to be expected. The amount of copper oxide which can be assimilated by one molecule of copper sulfate seems to be limited to about two molecules. The evidence furnished by the experiments is not sufficient to fix this limit beyond doubt, since the next higher amount of copper oxide used was four molecules to one of copper sulfate. Since, however, the salts produced in these cases contained large admixtures of unattacked copper oxide, and since the copper sulfate in the solutions was practically reduced to zero in all cases where two molecules of copper oxide to one of copper sulfate were used, and not where less than this amount was used, the presumption is very strong that this amount represents very closely the limit assimilable under the conditions of these experiments.

Another conspicuous fact shown by the results in Table III is that in all cases as the amount of copper oxide increases the amount of water decreases, and that as a limit the molecules of oxide and water to one of sulfate approach equality in the most basic salt, at the approximate value of two. In so far as is deducible from the evidence obtained in this investigation, the most basic salt which could be prepared by the method used would have approximately the formula  $\text{CuSO}_4 \cdot 2\text{CuO} \cdot 2\text{H}_2\text{O}$ . Whether there is a lower limit to the amount of copper oxide which may

be contained in a basic salt is not determinable from the evidence in hand, and remains a subject for further investigation.

In the literature, reference is made to several supposed salts which contain higher percentages of copper oxide than any that we have succeeded in obtaining. These salts were, however, invariably obtained by precipitations with alkaline reagents and the presumption is very strong that they were mixtures containing excess of hydroxide.

It is a well-known fact that ordinary solutions of copper sulfate are in general supersaturated with respect to basic sulfate, even though unsaturated with the normal sulfate. This is evidenced by the fact that prolonged standing or short boiling of such solutions results in the deposition of certain amounts of basic sulfates. It has been maintained that such basic sulfates show a definite composition, irrespective of the strength of the solutions from which they are prepared.<sup>1</sup> This point of view is maintained by Pickering in spite of serious lack of agreement in the results of his analyses. In order to convince ourselves upon this point the following experiments were carried out: Three bottles containing copper sulfate solutions of different strengths were prepared. The first contained a solution saturated at 80° diluted with five volumes of water; the second contained a solution which was saturated at 80° plus a considerable additional quantity of small crystals of copper sulfate, while the third contained solution saturated at 80° without any addition whatever. These bottles were placed in an electric oven and kept at 100° for a week, during which time they were frequently shaken. They were then removed, the contents quickly filtered and the basic sulfates (they are extremely insoluble) washed with water to remove excess of copper sulfate. These salts were dried and analyzed for copper. The results are given in Table IV.

TABLE IV.

Solution.	% CuO.
Sat. at 80° and diluted with 5 vols. water.....	66.34
Sat. at 80°.....	67.00
Sat. at 80° with $\approx$ $\text{CuSO}_4$ crystals.....	68.21

As is readily seen the composition of the basic sulfates prepared in this way is highly influenced by the concentration of the solutions from which they are prepared.

### Summary.

1. A considerable number of basic sulfates of copper were prepared by the direct action of copper oxide on solutions of copper sulfate, at three different temperatures.

2. The time required for such systems to attain equilibrium is about three months at 25° and about two weeks at 50°.

<sup>1</sup> Cf. Pickering, *Chem. News*, 47, 181.



3. Other conditions being constant, the composition of these basic sulfates is independent of the temperature of preparation within the range investigated.

4. The evidence obtained by a study of these salts makes it seem highly probable that they are not definite compounds, but rather are to be regarded as a three-component system in which all three components,  $\text{CuSO}_4$ ,  $\text{CuO}$  and  $\text{H}_2\text{O}$  (or if one prefers  $\text{CuO}$ ,  $\text{SO}_3$ ,  $\text{H}_2\text{O}$ ) are continuously variable within certain limits.

5. The evidence indicates that the maximum number of molecules of copper oxide that are capable of being taken up by one of copper sulfate is two, and that the formula for the most basic salt is probably quite close to  $\text{CuSO}_4 \cdot 2\text{CuO} \cdot 2\text{H}_2\text{O}$ .<sup>1</sup>

6. In salts of lower basicity the water content of the salt increases as the copper oxide content decreases, but there is as yet no evidence to show whether these changes continue throughout the whole range to normal  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ .

7. Basic copper sulfates prepared by heating copper sulfate and water together in varying relative amounts does not lead to the formation of definite compounds as has been maintained.

8. There is some evidence indicating the formation, under undetermined conditions, of a metastable series of basic sulfates.

9. In view of the above facts, it is only natural that the mineral Brochantite, should show a variable composition, depending on the conditions of its formation.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF KANSAS.]

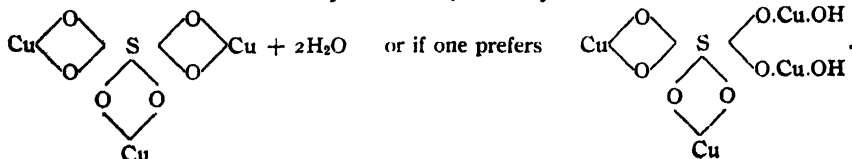
## CHLORIDES IN PRESENCE OF THIOCYANATES.

By F. W. BRUCKMILLER.

Received July 20, 1916.

Rosanoff and Hill<sup>2</sup> have shown that chlorides can be determined in the presence of thiocyanates by means of Volhard's method after the latter have been decomposed by concentrated nitric acid. This paper intends to show that chlorides can also be titrated with silver nitrate and chromate

<sup>1</sup> Professor W. A. Noyes has kindly called the authors' attention to the fact that this formula corresponds to that of the normal copper salt of orthosulfuric acid,  $\text{S}(\text{OH})_2$ , with two molecules of water of crystallization, and may be written



<sup>2</sup> THIS JOURNAL, 29, 1467 (1907).

indicator after the thiocyanates have been decomposed with nitric acid. Such a method is useful in water analysis where chlorides and thiocyanates occur together and it is desired to know only the chlorine content.

The solution containing the chlorides and thiocyanates is heated to boiling and concentrated nitric acid added drop by drop, the amount depending upon the thiocyanate present. If present in large quantities, nitric acid is added until the solution turns a light brown. For small quantities 2-3 cc. of nitric acid are sufficient. The solution is boiled for 15 minutes and filtered if necessary (free sulfur being precipitated if the concentration of thiocyanate is large) and after cooling is neutralized with normal  $\text{NaHCO}_3$ , using methyl orange as indicator. A little more than enough for neutralization is added, and after adding 1 cc. of chromate indicator, silver nitrate is added to the usual end point.

The method assumes (1) that the thiocyanate may be decomposed at  $100^\circ$  by such quantities of  $\text{HNO}_3$  as are insufficient to oxidize the chloride or cause volatilization of  $\text{HCl}$ ; (2) that all but traces of hydrocyanic acid formed during decomposition can be volatilized during the time required for oxidation; (3) that the sulfur is not present in such a form as to react with the  $\text{AgNO}_3$ ; (4) that the color of the methyl orange indicator does not interfere with the chromate end point.

Rosanoff has shown that no chlorine is lost as such, or as hydrochloric acid, in boiling the solution with nitric acid, and we have been able to confirm his conclusions. Varying amounts of sodium chloride were taken and boiled with varying quantities of nitric acid, and the solutions analyzed for chlorine before and after. The results in Table I show that no chlorine was lost during the operation.

TABLE I.—EFFECT OF NITRIC ACID ON SODIUM CHLORIDE SOLUTION AT  $100^\circ$ .  
Cc.  $\text{HNO}_3$ .

	1.	2.	3.	4.	5.
Volume 100 cc.					
NaCl before.....	0.0150	0.0150	0.0150	0.0150	0.0150
NaCl after.....	0.0149	0.0150	0.0151	0.0148	0.0148
Volume 50 cc.					
NaCl before.....	0.0150	0.0150	0.0150	0.0150	0.0150
NaCl after.....	0.0148	0.0149	0.0148	0.0151	0.0151
Volume 25 cc.					
NaCl before.....	0.0150	0.0150	0.0150	0.0150	0.0150
NaCl after.....	0.0150	0.0148	0.0147	0.0147	0.0147

In the decomposition of thiocyanate, hydrocyanic acid is one of the principal decomposition products. In pure solutions it is all removed by boiling, but in presence of chlorides a small quantity is always retained. In no case, however, was this amount larger than 3 mg. of CN per liter. This is not in accord with the work of Richards and Singer,<sup>1</sup> who find that larger quantities are retained. The complete removal

<sup>1</sup> *Am. Chem. J.*, 27, 208 (1902).

of the hydrocyanic acid is desirable, but traces do not interfere with the accuracy of the method. Even if 3 mg. per liter were always retained, the error in titrating chlorides in water analysis would be only 3 parts per million.

During decomposition the sulfur does not form any compound which in any way interfere with the titration with silver nitrate. No hydrogen sulfide was ever detected. Free sulfur forms if the concentration of thiocyanate is large. The exact products resulting were not determined, but, besides free sulfur, they are probably sulfate and complex organic compounds.

The presence of methyl orange in the solution gives a little different shade to the end point with chromate indicator but it is as easily duplicated and detected as is the color obtained in absence of methyl orange. Solutions of sodium chloride were titrated in presence and in the absence of methyl orange with the following results:

AgNO <sub>3</sub> with methyl orange (cc.).....	15.05	20.00	50.10	100.20
AgNO <sub>3</sub> without methyl orange (cc.)...	15.00	19.98	50.00	100.12

The solution is neutralized with sodium bicarbonate, instead of sodium hydroxide, to guard against an excess of hydroxyl ion in the solution with which silver nitrate reacts. An end point with the chromate indicator is obtained in a slightly acid solution but if considerable acid is present no end point is obtainable. The maximum concentration of (H<sup>+</sup>) allowable was determined and the results included in Table II.

To several solutions containing known quantities of chloride were added varying concentrations of sulfuric acid, beginning with 0.0004 N. Fifty cc. of each of these were titrated for chlorides according to the usual procedure.

TABLE II.—EFFECT OF ACID ON TITRATION OF CHLORIDES.  
Grams of Chlorine per Liter.

Conc. of H <sub>2</sub> SO <sub>4</sub> mols.	Present.	Found.	Present.	Found.	Present.	Found.	Present.	Found.
0.0002	0.026	0.026	0.084	0.084	0.104	0.104	0.206	0.206
0.0060	0.026	0.026	0.084	0.084	0.104	0.104	0.206	0.206
0.0010	0.026	0.026	0.084	0.084	0.104	0.104	0.206	0.206
0.0012	0.026	0.026	0.084	0.084	0.104	0.104	0.206	0.206
0.0014	0.026	0.026	0.084	0.084	0.104	0.104	0.206	0.206
0.0016	0.026	<sup>1</sup>	0.084	<sup>1</sup>	0.104	<sup>1</sup>	0.206	<sup>1</sup>

These results indicate that chlorides can be determined by titration in a 0.0014 M solution of sulfuric acid or a concentration of 0.0028 (H<sup>+</sup>), assuming that all of the acid is dissociated.

From these results we conclude that by decomposing the thiocyanates with hot nitric acid, chlorides can be determined volumetrically, using silver nitrate and chromate indicator.

LAWRENCE, KANSAS.

<sup>1</sup> No end point possible.

[CONTRIBUTION FROM THE CHEMICAL DEPARTMENT OF THE UNIVERSITY OF WISCONSIN.]

**THE CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE  
IN CERTAIN NONAQUEOUS SOLUTIONS.**

BY JAMES H. WALTON AND DEWITT O. JONES.

Received July 27, 1916.

The fact that aqueous solutions of hydrogen peroxide are extremely sensitive to the presence of foreign substances was recognized by Thenard,<sup>1</sup> who reached the conclusion that all substances exert some effect on this substance, some, like the acids, increasing its stability, others, like the finely divided metals and certain metallic oxides, tending to decompose it.

Concerning the stability of nonaqueous solutions of hydrogen peroxide towards foreign substances comparatively little is known. The metallic oxides, such as manganese dioxide and lead dioxide readily decompose ethereal solutions of the peroxide. To the knowledge of the authors, however, no data exist showing whether such soluble salts as the alkali iodides, which readily decompose hydrogen peroxide,<sup>2</sup> will show a similar action towards nonaqueous solutions of this substance.

**Experimental.**

In a series of experiments carried out by A. Brann,<sup>3</sup> it was found that ethereal solutions of the peroxide show absolutely no reaction when the following organic acids are dissolved in them: malic, picric, sulfanilic, citric, anthranilic, cinnamic, salicylic, gallic, camphoric, succinic, anisic, pyrogalllic, benzoic, oxalic, mono- and trichloroacetic, and stearic. The following are also without influence: acetamide, acetanilide, diphenyl amine, alloxan, *p*-toluidine, phenyl hydrazine, aniline, urethane, naphthalene,  $\beta$ -naphthylamine, nickel bromide, and the cobalt, calcium and cadmium salts of abietic acid. The following salts are soluble in ether, but they are decomposed when added to an ethereal solution of hydrogen peroxide, the decomposition being accompanied with the formation of a precipitate: cadmium iodide, ferric chloride, cupric chloride, copper oleate, and the abietates of silver, nickel, copper and manganese. The only ether soluble substance found that decomposed the ethereal solution of the peroxide catalytically, and without forming a precipitate, is lithium iodide. In this case the evolution of oxygen is copious.

Inasmuch as hydrogen peroxide is soluble in many other organic solvents,<sup>4</sup> and since many of these solvents dissolve some of the inorganic salts very readily, it was of interest to compare the activity of certain salts in nonaqueous and aqueous solutions of hydrogen peroxide. The following solvents were used: amyl acetate, amyl alcohol, isobutyl alcohol, and

<sup>1</sup> *Ann. chim. phys.*, **9**, 314 (1818).<sup>2</sup> Walton, *Z. physik. Chem.*, **47**, 2 (1904).<sup>3</sup> Dissertation, Wisconsin, 1914.<sup>4</sup> Walton and Lewis, *THIS JOURNAL*, **38**, 633 (1916).

quinoline. By shaking with the proper amounts of "perhydrol," solutions of the above were obtained, having concentrations of hydrogen peroxide varying from 1 to 3%. They also contained, of course, a small amount of water. In making an experiment, from 0.05 to 0.1 g. of the substance to be tested was dissolved in 5 cc. of the pure solvent. This was then added to the peroxide solution. If no gas was evolved the solution was carefully warmed. Table I gives the salts used and their behavior in the different solutions.

TABLE I.

The catalytic action of various inorganic salts on aqueous and certain nonaqueous solutions of hydrogen peroxide. D = vigorous decomposition; *d* = slight decomposition; N = no decomposition; *p* = precipitate formed.

	Water.	Amyl acetate.	Quinoline.	Isobutyl alcohol.	Amyl alcohol.
Cobalt acetate.....	D	D	..	D — <i>p</i>	D
Copper acetate.....	<i>p</i>	D — <i>p</i>	D	D — <i>p</i>	D — <i>p</i>
Lead acetate.....	D	D	D	D	D
Manganese acetate.....	D	D	D	D — <i>p</i>	D — <i>p</i>
Nickel acetate.....	D	D	..	D	D — <i>p</i>
Silver acetate.....	D	D	..	D	D
Cupric chloride.....	D	D	D	D — <i>p</i>	D
Ferric chloride.....	D	..	D	D — <i>p</i>	..
Manganese chloride.....	<i>d</i>	..	D	..	..
Mercuric chloride.....	N	..	N	N	..
Ammonium iodide.....	D	D	D	D	D
Cadmium iodide.....	D	D	..	D	D
Calcium iodide.....	D	..	D	D	D
Cuprous iodide.....	..	D	D	D	D
Lithium iodide.....	D	D	D	D	D
Manganese iodide.....	D	D — <i>p</i>	D	D	D
Mercuric iodide.....	..	N	N	N	N
Mercurous iodide.....	..	..	N	<i>d</i>	D
Potassium iodide.....	D	<i>d</i>	..	..	..
Sodium iodide.....	D	D	D	D	D
Strontium iodide.....	D	D	D	D	D
Lead nitrate.....	<i>d</i>	..	D	..	<i>d</i>
Mercuric nitrate.....	<i>d</i>	N	N	N	N
Silver nitrate.....	<i>d</i>	<i>d</i>	N	<i>d</i>	<i>d</i>
Cuprous cyanide.....	..	D	D	D	D
Mercuric cyanide.....	<i>d</i>	N	N	N	N
Mercuric bromide.....	N	N	N	N	N

The experiments show that in general those substances that act as catalyzers to hydrogen peroxide in aqueous solution are similarly active when the peroxide is dissolved in nonaqueous solvents.

The great solubility of hydrogen peroxide in quinoline is evidenced by

the fact that at  $0^{\circ}$  for certain concentrations the partition coefficient<sup>1</sup>  $\frac{\text{H}_2\text{O}_2 \text{ in water}}{\text{H}_2\text{O}_2 \text{ in quinoline}}$  may be as low as 0.276.

An investigation of the rate of decomposition of a peroxide solution in quinoline was undertaken. Manganese acetate was used as a catalyzer. To find out whether or not the catalytic decomposition of hydrogen peroxide in quinoline solution is quantitative, a solution of peroxide in quinoline was prepared and two 25 cc. portions placed in flasks. To one flask manganese acetate dissolved in quinoline was added, to the other an aqueous solution of potassium iodide and the solutions allowed to stand until no further decomposition took place. The volumes of oxygen liberated in each case were the same, 42.7 cc.

Proof that the amount of oxygen does not vary to any great extent with the amount of catalyzer is shown by the following data, the experiments being carried out in a manner similar to those just described:

Gram of manganese acetate per 26 cc. of solution.....	0.1	0.1	0.05	0.05
Oxygen evolved at $0^{\circ}$ and 760 mm.....	34.80	34.75	35.00	34.70

A series of measurements of the velocity of decomposition of hydrogen peroxide in quinoline solution at  $25^{\circ}$ , using manganese acetate as a catalyzer was carried out.

### Reagents.

**Quinoline.** The synthetic product was used. This was redistilled, the portion coming over between  $234^{\circ}$  and  $236^{\circ}$  being employed in the experiments.

**Manganese acetate.** The purest preparation of a standard make was used. It contains one molecule of water of crystallization.

The hydrogen peroxide was Merck's "Perhydrol."

The quinoline-peroxide solution was prepared by dissolving 6 cc. of 15% hydrogen peroxide in 250 cc. of the quinoline. This gave a solution that contains about 2.5% of water.

### Procedure.

In carrying out an experiment 25 cc. of this solution were placed in a flask (Fig. 1) and 1 cc. of a quinoline solution of manganese acetate placed in the capsule A. The reaction flask was then put in a thermostat kept at  $25^{\circ}$ ; it was connected with a gas buret and its contents allowed to come to the temperature of the bath. By turning the rod B, the capsule was dropped into the quinoline solution. The flask was then shaken, and

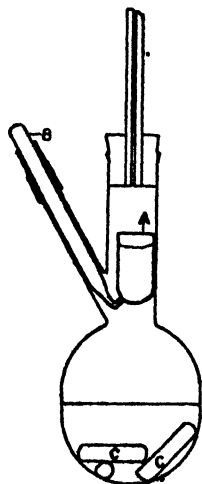


Fig. 1.

<sup>1</sup> Walton and Lewis, *loc. cit.*

the velocity of the decomposition of the peroxide determined by reading the volumes of oxygen in the gas burets. A number of pieces of glass rod, C, placed in the flask, increased the efficiency of the shaking apparatus.

In the following tables,  $t$  = time in minutes;  $x$  = vol. dry oxygen evolved at  $0^\circ$  and 760 mm.; A = total vol. oxygen evolved; C = g. catalyst in 26 cc. of solution;  $K_1$  = velocity constant for a monomolecular reaction;  $K_2$  = velocity constant for a bimolecular reaction.

TABLE II.

A = 41.2.		C = 0.005.	
$t$ .	$x$ .	$K_1$ .	$K_2$ .
3.4	9.3	0.0692	0.001865
4.9	11.8	0.0693	0.001778
6.6	14.3	0.0649	0.001770
9.2	18.0	0.0626	0.001825
11.7	20.7	0.0598	0.001845
18.9	25.7	0.0506	0.001805
22.5	27.4	0.0487	0.001787
27.3	29.5	0.0461	0.001830
30.8	30.2	0.0431	0.001752
32.1	31.2	0.0384	0.001884

Average  $K_2$  = 0.001814

TABLE III.

A = 35.0.		C = 0.005.	
$t$ .	$x$ .	$K_1$ .	$K_2$ .
3.2	6.9	0.0686	0.002193
4.7	9.7	0.0690	0.002331
6.2	12.2	0.0691	0.002466
9.2	16.5	0.0692	0.002770
10.7	18.2	0.0685	0.002893
12.7	20.3	0.0682	0.003107
14.7	22.2	0.0684	0.003371
17.7	24.5	0.0679	0.003766
20.7	26.5	0.0683	0.004302
24.7	28.5	0.0681	0.005071

Average  $K_1$  = 0.0685

The constants in Table II show clearly that under the conditions of the experiment the hydrogen peroxide decomposes according to the second order of reaction, and not according to the first order, as in aqueous solutions of this concentration.

This may also be shown as follows: Let  $C_1, C_2, C_3$ , represent solutions of hydrogen peroxide of different concentrations, and  $\theta_1, \theta_2, \theta_3$ , the time necessary for decomposing 50% of these solutions, respectively.

For a monomolecular reaction  $\theta_1 = \theta_2 = \theta_3$ , for a bimolecular reaction  $\theta_1, \theta_2, \theta_3$ , vary inversely as the concentration, that is

$$\theta.C = \text{const.} = k.$$

In the following table, concentrations and corresponding values of  $\theta$  both expressed as cubic centimeters of oxygen evolved, are given:

C.....	41.2	30.9	20.6
$\theta$ .....	11.6	15.5	22.3
$\theta.C$ .....	478.0	479.0	459.0

The constancy of the value  $\theta.C$  is a further proof that this reaction is bimolecular.

A repetition of this experiment gave a value of  $K_2$  = 0.001968, as against 0.001814 for the results given in Table II. The experiment was repeated, using a freshly prepared solution of peroxide in quinoline. The value of  $K_2$  this time was 0.001546. It was suspected that this difference might be due to different amounts of water in the quinoline, caused by different

conditions of pressure, etc., when purifying this substance. To eliminate this variable the quinoline was saturated with water at 25°, and the water-saturated quinoline used in all subsequent experiments.

The experiment just described was repeated, the conditions being identical with the exception that water-saturated quinoline was used. The results are recorded in Table III.

An inspection of the values computed for  $K_1$  and  $K_2$  shows that the reaction is now monomolecular. Apart from the constancy of their constants this is shown by the fact that the time necessary to decompose 50% of a quinoline-peroxide solution is independent of the concentration of the peroxide. This is shown by the following data:

C.....	35	30	20	15
$\theta$ .....	10	10	10.2	10.2
$\theta.C$ .....	350	300	204	153

The change from a bi- to a monomolecular reaction is of interest, and brings to mind\* the investigations of Dyer and Dale<sup>1</sup> and Bassett,<sup>2</sup> who showed that when hydrogen peroxide solutions of a greater concentration than 1/9 mol per liter are decomposed by colloidal platinum the reaction is bimolecular, whereas in dilute solutions it decomposes according to the first order. In this investigation there is, however, no change of concentration. The change of the reaction from a bi- to a monomolecular reaction is obviously brought about by saturating the quinoline with water.

Experiments similar to those described were carried out with different amounts of catalyzer. The following results were obtained:

	(1)	(2)	(3)	(4)	(5)	(6)
Gram manganese acetate per						
26 cc. of solution....	0.005	0.005	0.0025	0.0025	0.00125	0.00125
Time required to decompose						
50% of the $H_2O_2$ (minutes).	10.2	10.1	22.9	22.1	109.5	121.5

Decreasing the concentration of the catalyzer by 50% approximately decreases the speed of the reaction by the same amount. When the concentration is further decreased, however, the reaction is much slower, as is shown by comparison of Experiments 3 and 4 with 5 and 6. This is due primarily to a side reaction, in which some of the hydrogen peroxide is used up in oxidizing the quinoline. A quinoline-hydrogen peroxide solution can be kept for several days without any appreciable change. Addition of enough catalyzer to decompose the peroxide in a few minutes yields practically all the oxygen; if a small amount of catalyzer is added however, so that the experiment runs for two or three hours, only a part of the oxygen (about 75%) will be evolved; the rest is used up in oxidizing the quinoline. The manganese acetate not only catalyzes the peroxide

<sup>1</sup> *Proc. Chem. Soc.*, 29, 55 (1913).

<sup>2</sup> *Ibid.*, 29-30, 56 (1913).



decomposition, but it also catalyzes the oxidation of the quinoline by the peroxide.

In order to study the relation between the conductivity and the effect of the different concentrations of catalyzer, conductivity measurements were made at 25° with quinoline saturated with conductivity water at 25°, then with manganese acetate dissolved in 26 cc. portions of the solution in the concentrations in which it was used as a catalyzer in the experiments described. The results obtained are tabulated below:

Gram of manganese ace-

tate per 26 cc.....	0.00	0.00125	0.0025	0.005
Specific conductivity....	$2.3 \times 10^{-6}$	$3.4 \times 10^{-6}$	$3.75 \times 10^{-6}$	$5.2 \times 10^{-6}$

From these data it is evident that there is no simple relation between the conductivity of the solutions of manganese acetate in water-saturated quinoline and the velocity with which the peroxide solutions are decomposed in the presence of the corresponding amounts of manganese acetate.

#### Summary.

The results of this investigation may be briefly summarized as follows:

1. A number of compounds that decompose aqueous solutions of hydrogen peroxide catalytically are also active as catalyzers towards solutions of hydrogen peroxide in amyl alcohol, amyl acetate, isobutyl alcohol and quinoline.

2. Hydrogen peroxide in quinoline solution is decomposed quantitatively by manganese acetate. If the manganese acetate is present in so small a concentration that the reaction is slow, a side reaction, *viz.*, the oxidation of the quinoline by the hydrogen peroxide, is also appreciably catalyzed by the manganese acetate.

3. A solution of hydrogen peroxide in quinoline containing about 2% of water, when decomposed catalytically by manganese acetate, follows the second order of reaction. If the quinoline is saturated with water the reaction is monomolecular.

4. In solutions containing the catalyzer in high concentrations the velocity of reaction is approximately doubled by doubling the concentration of the catalyzer.

MADISON, WISCONSIN.

### [CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF PITTSBURGH.] STUDIES IN DIALYSIS. I. THE DIALYSIS OF A COLLOIDAL SOLUTION OF HYDROUS CHROMIC OXIDE IN CHROMIC CHLORIDE.<sup>1</sup>

By MARKS NEIDLE AND JACOB BARAB.

Received July 14, 1916.

In an effort to prepare the red form of colloidal chromic oxide<sup>2</sup> by pass-

<sup>1</sup> Presented at the Spring Meeting of the American Chemical Society, 1916.

<sup>2</sup> Woudstra, *Z. Chem. Ind. Kolloide*, **5**, 33 (1909).

ing steam through a chromic acetate solution and dialyzing with intermittent changing of the diffusate, it was found that the chromium continued to diffuse until none was left in the membrane. Analysis of the diffusate from a solution of hydrous chromic oxide in chromic chloride showed a ratio of chromium to chlorine considerably greater than for pure chromic chloride. Colloidal solutions of hydrous ferric oxide in ferric chloride<sup>1</sup> do not behave in this way. At the end of twenty-four hours the ratio of iron to chlorine is 56 : 137 or less than Fe : 3Cl; it diminishes very rapidly until the amount of iron which diffuses can no longer be detected.

With very few exceptions, the process of dialysis has been employed simply to obtain a colloidal solution as free from electrolytes as possible. The observation that, in the dialysis of colloidal solutions of hydrous chromic oxide, the chromium diffuses more rapidly than the chlorine, suggested that a quantitative study of the dialysis of such solutions might throw some light on the nature of colloidal solutions and also on the process of dialysis.

#### Preparation of Solution of Hydrous Chromic Oxide in Chromic Chloride.

—Analysis of a commercial "C. P." preparation<sup>2</sup> of chromic chloride in the form of a gluey mass, gave the following results: chromium, 100 equivalents ( $\frac{1}{3}$  Cr); chlorine, 90 equivalents (1 Cl); sulfate, 3.3 equivalents ( $\frac{1}{2}$  SO<sub>4</sub>). The sulfate was removed by precipitation with the calculated amount of barium chloride added to a boiling solution of the chromic chloride. The filtrate was greatly diluted, heated to boiling and treated with ammonium hydroxide. Boiling was continued until the odor of ammonia became very faint. The hydrous chromic oxide was allowed to settle, washed three times by decantation, and finally filtered on a Büchner funnel. The desired amount of this hydrous chromic oxide, which now gave no tests for sulfate, was dissolved in small portions in the calculated amount of boiling 6 *N* hydrochloric acid. To bring the last portions into solution it was necessary to evaporate the solution to a small bulk. The resulting colloidal solution was filtered, diluted to a convenient volume, and kept as a stock solution. Its composition was: chromium, 0.1610 gram-equivalents ( $\frac{1}{3}$  Cr); chlorine, 0.0786 gram-equivalents (1 Cl) per 100 cc.

**Continuous Dialysis.**—One hundred cubic centimeters of the colloidal solution were placed in a parchment paper membrane, set up as shown in the diagram, and adjusted so that the levels of liquid, inside and outside,

<sup>1</sup> Picton and Linder, *J. Chem. Soc.*, 87, 1908 (1905).

<sup>2</sup> As an instance of the reliability of the analysis on the labels of C. P. chemicals, the label on this preparation reads: CrCl<sub>3</sub> + ?H<sub>2</sub>O. H<sub>2</sub>S metals,..... "nil." Fe,..... 0.0023%. S,..... present. K,..... present.

were the same. By means of stopcock C the flow of distilled water was regulated to a rate of about 800 cc. per hour. At intervals the vessel F was removed and replaced by another. The volumes of the diffusates were measured and convenient portions taken for analysis. The results expressed in terms of milliequivalents are given in Columns 4 and 5, Table I.

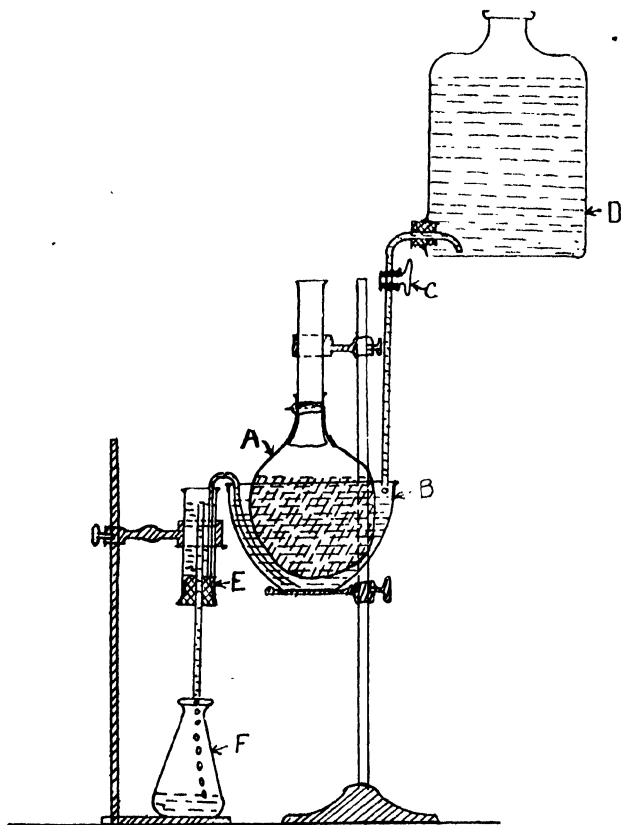


Fig. 1.

**Intermittent Dialysis.**—One hundred cubic centimeters of the stock solution were introduced into a parchment paper dialyser and suspended in a two-liter beaker containing 400 cc. of distilled water. The levels of the liquids on both sides of the membrane were practically the same initially. At the intervals given in Col. 3, Table II, the outer vessel was removed and another beaker containing 400 cc. of distilled water was placed in its stead.

**Dialysis without Changing Diffusate.**—Fifty cubic centimeters of the stock solution were placed in a parchment paper membrane and suspended in a liter beaker containing 400 cc. of distilled water. The dialysis was not disturbed except for the removal of samples from inside the membrane and from the diffusate for analysis. As no precaution was taken to prevent evaporation from the diffusate, its concentration is higher than it would have been if this precaution had been taken.

Each membrane was tested for leaks, at the conclusion as well as at the beginning of the experiment, by introducing colloidal hydrous ferric oxide and immersing in water. In no case did the colloidal hydrous ferric oxide pass through the membrane.

Unless specifically stated otherwise, the term "ratio" will mean the ratio in gram equivalents of chromium ( $1/3$  Cr) to chlorine (1 Cl).

TABLE I.—CONTINUOUS DIALYSIS.

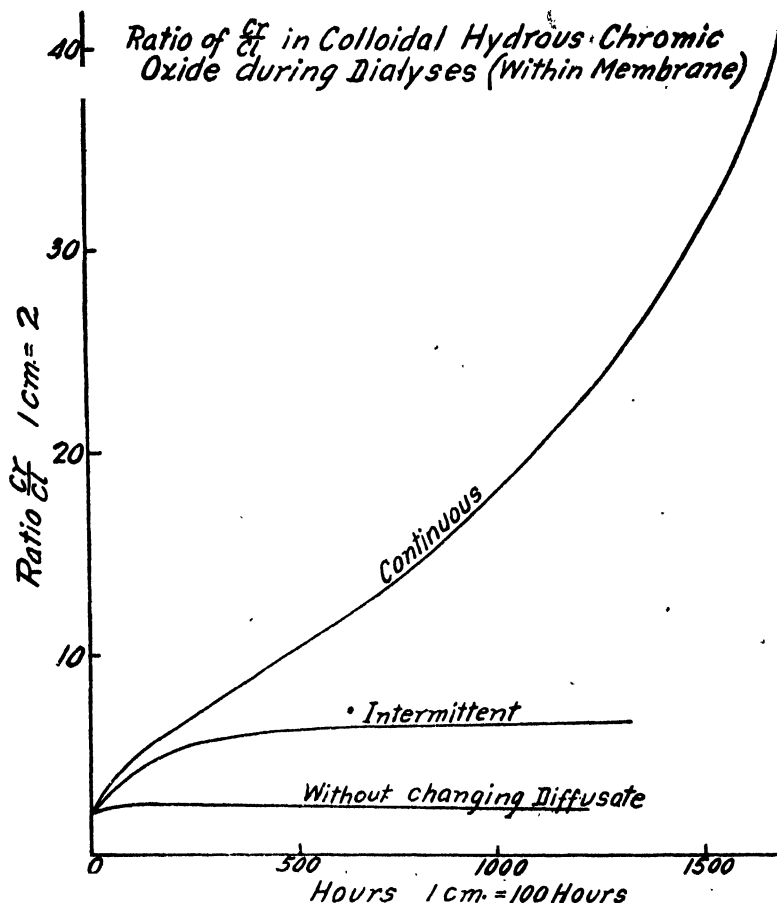
Interval number.	Total time. Hours.	Time interval. Hours.	Amounts diffused through membrane. Milliequivalents.		Rates of diffusion. Milliequivalents per hour.		Ratio Cr/Cl in diffusate.	Amounts remaining in membrane. Milliequivalents.		Ratio Cr/Cl within membrane.
			Chlorine.	Chromium.	Chlorine.	Chromium.		Chlorine.	Chromium.	
1	1/2	1/2	1.916	1.916	3.832	3.832	1.00	76.73	159.08	2.07
2	1	1/2	3.594	4.017	7.188	8.034	1.16	73.19	155.07	2.12
3	1 1/2	1/2	3.505	4.237	7.010	8.474	1.21	69.69	150.83	2.16
4	2	1/2	3.549	4.522	7.098	9.044	1.28	66.14	146.31	2.21
5	3	1	6.438	8.670	6.438	8.670	1.35	59.70	137.64	2.30
6	4	1	5.264	7.575	5.264	7.575	1.44	54.43	130.06	2.39
7	5	1	4.035	5.749	4.035	5.749	1.42	50.40	124.31	2.47
8	6	1	3.198	4.955	3.198	4.955	1.55	47.20	119.36	2.53
9	8	2	4.800	7.375	2.400	3.688	1.54	42.40	111.98	2.64
10	24	16	15.334	24.170	0.959	1.511	1.57	27.07	87.81	3.24
11	27	3	1.226	1.870	0.404	0.623	1.53	23.84	85.94	3.33
12	48	21	5.021	6.805	0.239	0.324	1.36	20.82	79.14	3.80
13	52	4	0.579	0.832	0.145	0.208	1.44	20.24	78.31	3.88
14	72	20	2.641	3.040	0.132	0.152	1.15	17.60	75.27	4.27
15	96	24	2.136	2.663	0.089	0.103	1.16	15.46	72.80	4.73
16	120	24	1.437	1.323	0.0611	0.0551	0.902	14.00	71.48	5.10
17	144	24	1.124	1.127	0.0468	0.0469	1.00	12.87	70.36	5.47
18	168	24	0.856	0.651	0.0356	0.0271	0.76	12.02	69.71	5.80
19	192	24	0.630	0.463	0.0263	0.0193	0.735	11.39	69.24	6.08
20	244	52	1.162	0.751	0.0223	0.0144	0.646	10.23	68.49	6.70
21	341 1/2	97 1/2	1.789	1.082	0.0183	0.0111	0.605	8.44	67.41	8.00
22	448 1/2	117 1/2	1.481	0.672	0.0127	0.0057	0.454	6.96	66.74	9.57
23	642	194	1.510	0.355	0.078	0.0018	0.235	5.45	66.38	11.98
24	834	192	0.874	0.134	0.0046	0.0007	0.153	4.57	66.25	14.50
25	1003	169	0.925	Trace	0.0055	....	...	3.65	66.25	18.10
26	1358	355	1.108	Trace	0.0031	....	...	2.54	66.25	26.06
27	1752	394	0.950	....	0.0024	....	...	1.59	66.25	41.60

TABLE II.—INTERMITTENT DIALYSIS.

Interval number.	Total time. Hours.	Time interval. Hours.	Amounts diffused through membrane. Milliequivalents.		Rates of diffusion. Milliequivalents per hour.		Ratio Cr/Cl in diffusate.	Amounts remaining in membrane. Milliequivalents.		Ratio Cr/Cl within membrane.
			Chlorine.	Chromium.	Chlorine.	Chromium.		Chlorine.	Chromium.	
A	1/3	1/3	2.911	1.916	8.733	5.748	0.66	75.69	158.08	2.06
B	5/6	1/2	3.357	2.611	6.714	5.222	0.78	72.33	155.47	2.15
C	1 1/3	1/2	3.416	2.910	6.832	5.820	0.85	68.92	152.56	2.22
D	2 1/3	1	6.003	5.299	6.003	5.299	0.88	62.91	147.26	2.36
E	4 1/3	2	7.437	9.001	3.719	4.500	1.21	55.48	138.06	2.49
F	17 1/2	13 1/4	15.005	26.003	1.131	1.962	1.73	40.47	112.06	2.77
G	20	2 1/2	2.523	3.114	1.001	1.245	1.23	37.95	108.95	2.87
H	41 1/2	21 1/2	6.280	12.200	0.292	0.567	1.94	31.67	96.75	3.05
I	44 1/2	3	1.497	1.602	0.499	0.534	1.07	30.17	95.14	3.15
J	47 1/2	3	1.343	1.526	0.488	0.509	1.13	28.83	93.62	3.25
K	65 1/2	18	3.532	5.868	0.196	0.326	1.66	25.30	87.75	3.47
L	69 1/2	4	1.123	1.674	0.281	0.419	1.49	24.17	86.08	3.56
M	73 1/2	4	1.191	1.808	0.298	0.452	1.52	22.98	84.27	3.66
N	89 1/2	16	2.637	6.194	0.165	0.387	2.35	20.35	78.17	3.84
O	93 1/2	4	0.958	1.751	0.240	0.438	1.83	19.39	76.42	3.94
P	114	20 1/2	3.443	10.415	0.168	0.507	3.12	15.94	66.01	4.14
Q	116	2	0.468	1.036	0.234	0.518	2.21	15.48	64.97	4.20
R	138	22	3.098	10.425	0.141	0.474	3.36	12.38	54.55	4.41
S	142	4	0.432	0.518	0.108	0.130	1.20	11.94	54.02	4.54
T	146	4	0.366	0.383	0.092	0.096	1.05	11.58	53.75	4.65
U	162	16	0.627	1.044	0.039	0.065	1.66	10.95	52.70	4.81
V	170	8	0.576	1.403	0.073	0.175	2.44	10.38	51.30	4.93
W	186	16	1.275	5.122	0.080	0.321	4.02	9.10	46.18	5.08
X	189	3	0.284	0.765	0.095	0.255	2.70	8.82	45.41	5.15
Y	234	45	2.162	9.509	0.048	0.211	4.39	6.65	35.90	5.40
Z	330	96	2.142	10.800	0.0223	0.1125	5.03	4.21	23.63	5.63
A'	354	24	0.544	2.021	0.0227	0.0842	3.72	3.66	21.60	5.89
B'	667	312	1.620	8.700	0.0052	0.0279	5.68	2.04	12.90	6.31
C'	1339	672	0.943	5.656	0.0014	0.0084	6.00	1.10	7.25	6.58

TABLE III.—DIALYSIS WITHOUT CHANGING DIFFUSATE.  
COLLOID.

Sample number.	Time. Total.	Interval time.	Cc. sample.	Milli-equivalents. Chlorine.	Milli-equivalents. Chromium.	Ratio Cr/Cl.
1	48	48	..	.....	.....	.....
2	96	48	5	0.541	1.343	2.58
3	172	76 1/2	5	0.482	1.229	2.55
4	285	113	10	0.962	2.424	2.52
5	538	253	10	1.075	2.487	2.31
6	1232	694	10	1.409	3.114	2.21
DIFFUSATE.						
1	48	48	10	1.199	1.677	1.40
2	96	48	10	0.800	1.380	1.73
3	172	76 1/2	10	0.809	1.485	1.835
4	285	113	10	0.844	1.612	1.910
5	538	253	10	0.991	1.942	1.960
6	1232	694	10	1.337	2.653	1.985



### Observations on Results.

#### I. Continuous Dialysis.

- a. At the end of the first interval, the ratio in the diffusate was 1, or the same as in chromic chloride.
- b. This ratio increased to 1.57 without abrupt changes, and then decreased continuously to zero.
- c. The ratio within the membrane increased continuously from 2.05 to 41.6. (See curve.)
- d. More than three-quarters of the colloidal hydrated chromic oxide remained in the membrane at the end of the dialysis, when the chromium had ceased to diffuse.

#### II. Intermittent Dialysis.

- a. The ratio in the diffusate at the end of the first interval was 0.66 and was less than 1 for the three following intervals.

b. After the first four intervals the ratio was always greater than 1.

c. While there are considerable irregularities, it is evident that, in general, the ratio in the diffusate is greater the longer the interval of dialysis.

d. The ratio in the membrane, at the start, increased fairly rapidly, but very slowly after the first 400 hours. At the end of 1300 hours, the ratio in the membrane was only 6.58, *i. e.*, only slightly greater than in the diffusate. (See curve.)

e. At the conclusion of the dialysis less than one-sixteenth of the colloidal hydrous chromic oxide remained in the membrane, and the chromium had not yet ceased to diffuse.

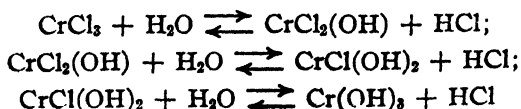
### III. Dialysis without Changing Diffusate.

a. The ratio of Cr to Cl in the diffusate rose rather rapidly during the first 96 hours, and then more slowly, gradually approaching the value within the membrane. (See curve.)

### Interpretation of Results.

The first point which must be decided is whether the diffusates, with ratios greater than one, contain a basic chloride of chromium, or colloidal hydrous chromic oxide. It is noteworthy that the basic chlorides recorded in Gmelin-Kraut are all noncrystalline, and their compositions suggest either a mixture of simpler compounds or colloidal complexes. The existence of basic chlorides of chromium as true chemical individuals, has not been positively demonstrated. Hence we will assume that all diffusates with ratios greater than one, contain colloidal hydrous chromic oxide. This assumption is supported by the fact that these diffusates give a gel on evaporation, and, when the ratio is appreciably greater than one, yield a precipitate with potassium sulfate.

A striking difference between continuous and intermittent dialysis, as conducted in this work, is that in the former the colloidal particles finally cease to pass through the membrane, while in the latter it is seen that, after dialysis for 56 days, they continue to diffuse. A plausible as well as simple explanation of this strange behavior is that in continuous dialysis, the colloidal particles grow in size until they are too large to pass through the membrane, but in the intermittent dialysis they do not grow to such a size. We will now attempt to account for our observations on the basis of the prevailing theory of colloids, which maintains that the particles in a colloidal solution are polymers of the simplest molecule, with all the constituents in the dispersion medium more or less adsorbed. Chromic chloride in aqueous solution is hydrolyzed according to the following equations:



The addition of hydrous chromic oxide will change these equilibria somewhat, but all the substances in the above equations and the ions into which they dissociate will be present in our stock solution—in true solution in the dispersion medium and adsorbed in the disperse phase. The charges on the colloidal particles and their stability are due to the adsorption of an excess of positive ions.

**The Ratios of Chromium to Chlorine in the Diffusate.**—The rates of dialysis of the various solutes contained in a membrane immersed in water will, at the start, be proportional to the diffusion constants and to the molar concentrations. For simplicity, the solutes in the original solution will be taken as follows: colloid, chromic chloride, hydrochloric acid, and an excess of chloride ion, whose negative charge is equivalent to the positive charge on the colloidal particles. The excess of chloride ion in the dispersion medium is practically a part of the colloid and therefore will not be considered separately in the following treatment. The order of the diffusion constants is: hydrochloric acid (highest), chromic chloride, colloid (lowest). At the beginning of the dialysis, in view of the difference in their diffusion constants, we will expect in the diffusate a greater ratio of hydrochloric acid to chromic chloride than exists within the membrane in the dispersion medium, and in a short interval very little of the colloid will have diffused. Thus we may explain the low ratios in the diffusates in intermittent dialysis for the first four intervals, which are short.

An increase in the molar concentration of colloid relatively to the solutes in the dispersion medium will result in a greater relative diffusion of the colloid. The initial rapid diffusion of chromic chloride and hydrochloric acid will greatly reduce their effective concentrations in a short time, and again the relative diffusion of colloid will increase. A greater relative diffusion of colloid means a greater ratio in the diffusate. Both of the above effects exert particular influence in intermittent dialysis, the more so the longer the interval. Hence, for intermittent dialysis, the longer the interval, the greater the ratio in the diffusate.

A ratio in the diffusate less than that in the membrane will lead to a greater relative molar concentration of the colloid in the membrane, if the colloidal particles remain of the same size, *i. e.*, if the molecular weight of the colloid does not increase. Growth of the particles will have the opposite effect, not only diminishing the relative molar concentration but also the diffusion constant of the colloid.

In the continuous dialysis, the constant flow of distilled water maintains fairly uniform, or uniformly changing conditions in the diffusate, and therefore the results are far more regular than in the intermittent process. As the dialysis progresses, the ratio in the diffusate increases because the molar concentration of the colloid relatively to the solutes



in the dispersion medium increases. Since the relative concentration of the colloid in grams per liter increases throughout, the ratio in the diffusate must continue to increase unless the particles grow larger. From Interval 10, Table I, the ratio in the diffusate begins to decrease, and furthermore, the increase of this ratio from Intervals 1 to 10 is insufficient to account for the increase in the relative concentration of the colloid. Hence the data in Table I indicate that continuous dialysis is accompanied by a continuous growth of the particles.

Little need be said concerning the dialysis without changing the diffusate. It is evident that osmotic equilibrium is established in a relatively short time, while the establishment of complete uniformity between internal and external liquids takes place very slowly.

### Mechanism of the Growth of the Particles.

Two distinct processes are probably involved in the growth of the particles: first, aggregation of particles to form larger ones; second, a gradual increase of the hydrous chromic oxide in the nuclei of the particles due to hydrolysis of the chromic chloride adsorbed.

Aggregation of the particles may be explained on the basis of Bredig's theory of colloid precipitation, according to which a decrease of the potential between disperse phase and dispersion medium will cause an increase in the surface tension of the latter at its interface with the former. This increase in surface tension is conducive to aggregation. As the concentration of electrolyte in the dispersion medium relatively to the colloid diminishes during dialysis, the excess of positive ions adsorbed by the particles decreases. Thus the potential between disperse phase and dispersion medium is lowered continuously, and aggregation takes place continuously.

The large amount of water adsorbed is in no small measure responsible for the size of colloidal particles of hydrous oxides. It is also likely that adsorbed electrolytes greatly diminish the proportion of adsorbed water. Thus diffusion of adsorbed electrolytes, particularly hydrochloric acid, from disperse phase into dispersion medium, during dialysis, may result in a growth of the particles: first, by increasing the adsorbed water, and second, by progressive hydrolysis of the adsorbed chromic chloride by the adsorbed water. In the latter the chromic hydroxide formed becomes part of the nuclei.

### Summary.

1. In intermittent or continuous dialysis, in a parchment paper membrane, of a solution of hydrous chromic oxide in chromic chloride, the colloidal particles diffuse through the membrane.

2. In intermittent dialysis the ratio of chromium ( $1/3$  Cr) to chlorine (1 Cl) in the diffusate after a short time is always greater than one. In general, it is greater the longer the interval of dialysis for the same diffusate.

3. In continuous dialysis, the ratio of chromium to chlorine in the diffusate increases from 1 to a maximum of 1.57, then gradually diminishes and approaches zero.

4. In intermittent dialysis, as conducted in this research, about 6% of the original colloid, still associated with considerable electrolyte, remains in the membrane at the end of 56 days, and colloid still diffuses. This dialysis could have been continued until no colloid remained within the membrane.

5. In the continuous dialysis, 75% of the original colloid remains in the membrane. Continuing the process beyond 35 days, increases the purity of the colloid without loss of chromium, *i. e.*, only hydrochloric acid diffuses.

6. If the intervals in intermittent dialysis are made smaller, more satisfactory results are to be expected. In fact, by conducting the entire process in very short intervals, the efficiency may even exceed that of continuous dialysis. The latter procedure, however, is impractical.

7. The variations of the ratios of chromium to chlorine in the diffusates are accounted for. They indicate a gradual growth of the particles. In the intermittent process, the particles did not grow sufficiently to be retained by the membrane, whereas in continuous dialysis they did.

8. The growth of the particles is explained partly by aid of Bredig's theory of colloid precipitation and partly by assuming that the nuclei of the particles grow as the adsorbed chromic chloride is hydrolyzed by the adsorbed water.

PITTSBURGH, PA.

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[CONTRIBUTION FROM THE SEVERANCE CHEMICAL LABORATORY OF OBERLIN COLLEGE.]

## THE COLLOIDAL ARSENATES AND PHOSPHATES OF IRON.

BY HARRY N. HOLMES AND R. E. RINDFUSZ.

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The usual method of analysis of sulfide ores requires the dissolving of the sample in aqua regia and the addition of potassium chlorate or bromine to oxidize separated sulfur. After evaporation to dryness, addition of hydrochloric acid, filtration and treatment of the filtrate with ammonium hydroxide, any iron present is precipitated as ferric hydroxide. if

In attempting to apply this method to arsenopyrite, as directed by Olsen,<sup>1</sup> we failed to get the expected precipitate of ferric hydroxide. Instead a rich red solution resulted.

Assuming that ferric orthoarsenate was formed in the process, we attempted to duplicate the final result by mixing solutions of ferric chloride and disodium arsenate and treating the precipitate thus formed with

<sup>1</sup> Olsen's *Quant. Chem. Anal.*, 4th Ed., p. 172.

ammonium hydroxide. The same red solution resulted and, upon dialysis, we found it to be colloidal.

A search of the literature showed that Grimaux<sup>1</sup> had made colloidal ferric arsenate by the ammonium hydroxide peptization of precipitated ferric arsenate and, in similar manner, colloidal ferric phosphate. E. A. Schneider<sup>2</sup> also contributed something in this field but the two writers did little more than start the work.

We planned a more thorough study of the colloidal arsenates and phosphates of iron but at the very beginning found a serious difficulty. On treating ferric chloride solution with a solution of disodium orthoarsenate a rather gelatinous precipitate of  $\text{Fe}_2(\text{HAsO}_4)_3$  forms. This formula is also written  $2\text{Fe}_2\text{O}_3 \cdot (3\text{As}_2\text{O}_5) \cdot 3\text{H}_2\text{O}$ . Ordinary methods of washing failed to remove adsorbed ions. One sample washed "thoroughly" in the usual manner until the washings showed only a trace of excess arsenate was set away under water for four months. This water then contained so much soluble arsenate that it seemed as if the original precipitate had not been washed at all.

The problem of purifying the semigelatinous precipitates of ferric arsenate and phosphate was finally solved satisfactorily by mechanical disintegration of the wet precipitates. The results of that part of our investigation cast some doubt on the accuracy of many formulas given in the literature for the various phosphates of iron. Different degrees of washing precipitates that so strongly adsorb ions must certainly have given analytical evidence for many different formulas. Possibly this same doubt may extend to analysis in other fields. It was our custom to prepare the precipitate for peptization by adding a slight excess of a solution of disodium arsenate, for example, to a solution of ferric chloride and then removing this excess of soluble arsenate as well as the soluble salt formed by the reaction. The method we used has been described elsewhere.<sup>3</sup>

**Peptization by Ammonium Hydroxide.**—As observed by Grimaux,<sup>4</sup> the insoluble orthoarsenate and orthophosphate of ferric iron are quickly peptized by ammonium hydroxide into red colloids. In dilute ammonium hydroxide the action is slower, but in any case may be hastened by shaking. Several attempts to utilize the full power of a definite weight of ammonium hydroxide in peptization gave us interesting results. A sample of 24 cc. of the wet paste of ferric arsenate was shaken with 2 cc. of concentrated ammonium hydroxide in a stoppered vessel and, after a week of occasional shaking, was completely converted into a deep red sol.

<sup>1</sup> *Compt. rend.*, 98, 1540 (1884).

<sup>2</sup> *Z. anorg. Chem.*, 5, 84 (1893); 7, 386 (1895).

<sup>3</sup> *J. Phys. Chem.*, 20, 522 (1916).

<sup>4</sup> *Loc. cit*

After standing in a tightly corked tube several months the liquid turned into a smooth solid butter of yellow-red color. Other samples acted in the same way. One, left open after treatment with concentrated ammonia, soon deposited considerable sediment, not of a buttery character. Of course this was caused by a rather rapid escape of ammonia. Approximately quantitative experiments indicated that 1 cc. of concentrated ammonium hydroxide peptizes an amount of wet paste equivalent to 1 g. of ferric arsenate. This corresponds to about 15% more ammonium hydroxide than is enough to replace the remaining hydrogens of the  $\text{Fe}_2(\text{HAsO}_4)_3$ .

Wittstein<sup>1</sup> observed that ferric phosphate could not be peptized by ammonium hydroxide unless disodium phosphate was present. We found no difficulty whatever in peptizing the thoroughly washed precipitate of ferric phosphate.

During dialysis of the two colloids mentioned, considerable osmotic pressure developed. One sample of ferric arsenate sol rose, in a few weeks, to a level of 9.5 cm. above the water outside the dialyzing tube. After some time this dropped rather rapidly, not, however, because of any break in the dialyzing membrane (goldbeater's skin). It would seem that this action may have been influenced by changes in the size of the colloidal aggregates through removal of ions and instability of phases. Not long after the fall in osmotic pressure small lumps of gel appeared.

Ammonia was gradually removed during dialysis and the dialysates for some time showed a test for arsenate ion. This removal of ammonium arsenate is discussed in detail under the heading "Properties of the Colloid." After continued dialysis for a few months the sol of ferric arsenate formed an excellent dark red gel. Grimaux failed to obtain this gel. In a small dialyzer the gel was solid and like a good fruit jelly in texture but in a large dialyzer the gel was lumpy, possibly due to greater agitation in changing the water. This gel could not be peptized again by ammonium hydroxide. When dissolved in hydrochloric or nitric acid and dialyzed a poor gel resulted.

From this point on we will discuss ferric arsenate, but it is to be noted that all results, unless otherwise stated, were duplicated with ferric phosphate.

**Properties of the Colloids.**—The sol of ferric arsenate is quite like colloidal ferric hydroxide (or "hydrated ferric oxide") in appearance, varying from a light cherry to a black-red with increase in concentration. The question arose whether this is not, after all, merely colloidal ferric hydroxide with adsorbed arsenate. Experiments readily showed that the colloid was negatively charged whereas colloidal ferric hydroxide is positive. Subjected to prolonged electrolysis in a 25 cm. tube with 18

<sup>1</sup> Comey's "Dictionary Chem. Solubilities," p. 304.

volts and less than 0.1 ampere current the red particles migrated to the positive pole and coagulated. Furthermore the ferric arsenate sol was extremely sensitive to an increase in valence of positive ions while an increase in valence of negative ions was without effect, a simple proof of the negative nature of the colloid. There was no difference in the amount of 0.02 *N* sodium chloride or 0.02 *N* disodium phosphate needed for coagulation of the colloid. Evidently the trivalent negative phosphate ion exerted just as little coagulating power as did the univalent negative chloride ion. On the other hand coagulation was produced by much less 0.02 *N* barium chloride and by very much less 0.02 *N* aluminium chloride.

The well-dialyzed sol of ferric arsenate is quite stable. One sample, over a year old at this date, shows no sign of settling. It is not coagulated by boiling but is very sensitive to polyvalent positive ions and is coagulated by considerable alcohol. A very little nitric or hydrochloric acid produces a coagulum, but this dissolves easily in a slight excess of the acid. Unless very dilute acid is used and added slowly no coagulum shows but the deep red color turns to the light yellow of a ferric chloride solution. Addition of excess ammonium hydroxide to this solution gives a precipitate, apparently ferric hydroxide, leaving a colorless liquid above. This point is discussed later. Evaporated spontaneously in the air the colloid is not reversible.

The thoroughly dialyzed colloid contains no free ammonia and on heating with sodium hydroxide not enough combined ammonia is released to affect litmus. Dialyzed colloidal ferric arsenate was evaporated to dryness on the water bath and duplicate samples analyzed. No. 1 contained 38.0% iron and 15.8% arsenic; No. 2 contained 38.3% iron and 15.6% arsenic. These values correspond to the formula  $\text{FeAsO}_4 \cdot \text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$  which might be called basic ferric orthoarsenate. Another sample prepared at a different time was dialyzed until lumps of gel appeared. The mixture of sol and gel was analyzed for the ratio of iron to arsenic, which was found in satisfactory agreement with the above formula. The removal of soluble arsenate, doubtless as ammonium arsenate as previously mentioned, accounts for the change in formula from  $\text{Fe}_2(\text{HASO}_4)_3$  of the fresh precipitate to  $\text{FeAsO}_4 \cdot \text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$  of the dialyzed colloid. It was suggested by W. Metcalf that the original precipitate was decomposed by water, thus accounting for the change in composition on dialysis. Lachowicz<sup>1</sup> states that such is the case. However, our precipitate after the special purification previously mentioned was kept under distilled water three months and this water gave no test for arsenate ion and only a slight test for chloride ion. It seems probable, therefore, that this precipitate is not decomposed by water and that Lachowicz's observation must have applied to an incompletely washed precipitate.

<sup>1</sup> *Sitzb. kais. Akad. Wiss., Wien.*, 101, IIb, 374.

### Absorptive Power of the Colloids.

Ferric hydroxide was dissolved in a solution of ferric chloride in order to obtain colloidal ferric hydroxide and ferric ions in the same solution. Without dialyzing, this was treated with a solution of sodium arsenate. The white precipitate of ferric arsenate appeared an instant before the red coagulum of ferric hydroxide. Naturally the trivalent negative arsenate ions neutralized the positive charge on the colloidal ferric hydroxide and coagulation followed. But at the same time ferric ions from the ferric chloride reacted with arsenate ions to precipitate white ferric arsenate. This simultaneous precipitation and coagulation insured an intimate mixture of the insoluble ferric hydroxide and ferric arsenate. The entire precipitate was readily peptized by addition of ammonium hydroxide into a deep red sol.

The peptizing action of ammonium hydroxide on ferric arsenate has already been discussed, but even an excess of this base has no such effect on precipitated ferric hydroxide. The ferric hydroxide precipitate has simply been adsorbed by the colloidal ferric arsenate and thus carried into suspension. To test this point further a finely divided precipitate of ferric hydroxide was shaken in water with an excess of finely divided precipitate of ferric arsenate. Addition of ammonium hydroxide formed an excellent sol of unusually deep red color and with a greenish "bloom." A small amount of sediment slowly settled on standing. This deep color and bloom were duplicated by adding very little colloidal ferric hydroxide—less than enough for mutual precipitation—to the dialyzed ferric arsenate. The bloom was apparently due to the presence of aggregates somewhat larger than those of the clearer colloids.

The above experiments furnish further evidence that colloidal ferric arsenate is not colloidal ferric hydroxide with adsorbed arsenate. We have loaded our negative colloid with a positive colloid, ferric hydroxide, up to a point short of complete discharge. When that limit is reached adsorption ceases and precipitation results.

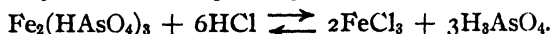
Ferric chloride solution, as discussed later, dissolves precipitated ferric arsenate. If less than one-tenth enough to dissolve the precipitate is added the further addition of ammonium hydroxide forms a red colloid. Of course the ammonium hydroxide peptizes the ferric arsenate and at the same time forms some ferric hydroxide which is adsorbed by the colloidal ferric arsenate. If more than enough ferric chloride to peptize the arsenate is added there is some precipitation with ammonium hydroxide, but a red sol may also form. If still more ferric chloride is used, addition of ammonium hydroxide may cause complete precipitation, leaving a colorless liquid above. The excess ferric hydroxide, if formed first as a positive colloid, has coagulated the negative colloid, ferric arsenate, formed at the same time. Less than enough ferric hydroxide to discharge com-

pletely the negative colloid results in the adsorption of the ferric hydroxide and little or no precipitation.

This phenomenon, also observed in the adsorption of aluminium hydroxide and other hydroxides by colloidal ferric arsenate, is similar to that reported by Fisher and Herz.<sup>1</sup> They found that if, in a mixture of solutions of ferric and chromium salts, the chromium salt is in large excess, the addition of an excess of a solution of sodium hydroxide forms colloidal chromium hydroxide carrying into the sol all the iron as adsorbed ferric hydroxide. With a much smaller excess of the chromium salt both sol and precipitate may result while if the ferric salt is in excess there is no sol but complete precipitation.

We found other examples of hydroxide adsorption. A small amount of a solution of aluminium chloride was added to an excess of precipitated ferric arsenate and upon addition of ammonium hydroxide a sol resulted with no precipitation. An excess of aluminium chloride resulted in complete precipitation. Chromium chloride and lead nitrate were substituted for the aluminium chloride with similar results.

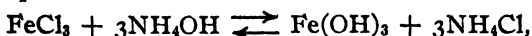
These adsorption experiments lead to an explanation of the fact that dialyzed colloidal ferric arsenate treated with excess hydrochloric or nitric acid yields a precipitate when ammonium hydroxide is added. In this case the ammonium hydroxide does not exert its usual peptizing action. If a fresh precipitate of  $\text{Fe}_2(\text{HAsO}_4)_3$  is dissolved in hydrochloric or nitric acid and ammonium hydroxide added the same precipitation results with some sol remaining. If considerable excess arsenic acid is mixed with ferric chloride solution and excess ammonium hydroxide added, both the white insoluble ferric arsenate and the red insoluble ferric hydroxide are seen. On shaking a deep red sol forms. If a smaller amount of arsenic acid is used the addition of ammonium hydroxide precipitates ferric hydroxide with possibly a little of the sol remaining.



In the equilibrium indicated above most of the iron is on the right of the equation. Addition of ammonium hydroxide must neutralize the hydrochloric acid and thus disturb the equilibrium to the left, causing the appearance of white insoluble ferric arsenate. At the same time ammonium arsenate is formed but this reacts readily with ferric chloride to form more ferric arsenate. Some ferric hydroxide must also be formed by the action of the base. An excess of ammonium hydroxide may peptize the white precipitate of ferric arsenate into a red colloid. However, unless considerable excess of arsenic acid is used any colloidal ferric arsenate formed is adsorbed and precipitated, at least in part, by the coagulum of ferric hydroxide. This needed excess of arsenic acid is not obtained when a precipitate of  $\text{Fe}_2(\text{HAsO}_4)_3$  is dissolved in hydrochloric

<sup>1</sup> *Z. anorg. Chem.*, 31, 352 (1902).

acid but it must be added. The ability of peptized ferric arsenate to adsorb ferric hydroxide is limited, as previously stated. It is also probable that the equilibrium



is shifted to the left by the action of excess arsenate ion on the ferric ion.

In the case of the dialyzed sol,  $\text{FeAsO}_4 \cdot \text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ , treated with hydrochloric acid the excess of ferric chloride over the arsenic acid formed is too great to yield a colloid on treatment with ammonium hydroxide. In other words, the ratio of three atomic weights of iron to one of arsenic gives too great an excess of ferric chloride when dissolved in hydrochloric acid. This is the ratio in the dialyzed colloid but it must be remembered that this is not the ratio of iron to arsenic that existed when the sol was formed in the presence of ions. That ratio was represented by the formula  $\text{Fe}_2(\text{HASO}_4)_3$  and the change to  $\text{Fe}_2\text{AsO}_4 \cdot \text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$  came about slowly as the ions dialyzed out.

**Peptization by Substituted Ammonias and Other Bases.**—A water solution of pure methyl amine quickly converted the precipitate of ferric arsenate into the characteristic dark red colloid. On dialysis a firm red gel formed after a few weeks. Aqueous solutions of dimethylamine and tetramethyl ammonium hydroxide showed just as great peptizing power, but the action of our trimethyl amine was much less marked. To vary the series of substituted ammonias we used diethyl amine with success. Aniline and pyridine were shaken with the wet precipitates but with little or no result.

Sodium hydroxide or potassium hydroxide solutions, carefully used, peptized ferric arsenate to a red sol, contrary to the statements of Grimaux. Very dilute base, about 0.1 *N*, must be added, drop by drop, with shaking, and great care taken to avoid an excess. Otherwise the colloid is precipitated as fast as formed. Doubtless such a lack of caution accounts for Grimaux' failure to obtain the colloid by sodium hydroxide peptization. Dialysis yields a rough coagulum rather than a compact gel.

Attempts to employ calcium hydroxide or barium hydroxide as peptizing agents failed, although the white precipitate of ferric arsenate developed a red tint. If there was an intermediate colloidal state it was not apparent, for the bivalent positive ions quickly coagulated the negative colloid. Solutions of sodium carbonate and ammonium carbonate showed a slight peptizing power.

These results suggest the possibility that the hydroxyl ion is a peptizing agent.

**Peptization by Ferric Chloride.**—Grimaux<sup>1</sup> states that a ferric chloride solution dissolves precipitated ferric arsenate and that, on prolonged

<sup>1</sup> *Loc. cit.*



dialysis, a transparent reddish yellow gel is formed. He did not pursue this line of investigation, not even experimenting with ferric phosphate.

We duplicated his work in making the sol and gel of ferric arsenate and obtained similar results with ferric phosphate. Grimaux records a difference in color of the ferric arsenate precipitated from ferric chloride, depending on whether sodium or potassium arsenate was used, the latter, he observes, giving a yellower precipitate. We found no such difference when care was taken to use a slight excess of the alkali arsenate. However, a very slight excess of ferric chloride exerts a peptizing action, developing a yellow to red tint. This, doubtless, accounts for the difference in color observed by Grimaux.

The amount of ferric arsenate peptized by ferric chloride solution is greatly increased by heating and the sol is a deeper red. Such a sol is not so stable and coagulates, in part, on dialysis.

The fact that ferric arsenate is so easily peptized by ferric chloride is good reason for using a slight excess of disodium arsenate solution on a solution of ferric chloride in preparing the precipitate. This excess of disodium arsenate can be removed by the method previously described.

The gel formed by the peptization of ferric arsenate by a solution of ferric chloride and subsequent dialysis is of excellent texture and looks much like a good fruit jelly. A sample retained its shape for several months when placed in 95% alcohol. Exposed to the air it dries down to a coarse powder. On standing sealed the gel slowly contracts. A change to a less hydrated phase is shown by the appearance of water around the gel. One gel had stood in a sealed tube for three months and had squeezed out considerable water. The water was rich in hydrochloric acid but gave only a slight test for iron. This shows that ferric chloride, included in the gel, had been hydrolyzed, the resulting colloidal ferric hydroxide being adsorbed, while the hydrochloric acid readily diffused throughout the water. Of course longer dialysis would have removed more of the hydrochloric acid. The gel may be dissolved in ammonium hydroxide to the characteristic sol which behaves exactly like that formed by the ammonium hydroxide peptization of ferric arsenate. It forms a good gel on dialysis and may then be redissolved in ferric chloride and a second gel formed on dialysis. A better structure of gel is secured if the ferric arsenate is peptized by ferric chloride solution immediately after precipitation. Delay from any cause, washing or otherwise, seems to permit an unfavorable change in physical condition. The gel forms after about two weeks' dialysis.

We next tried treating the precipitates of the arsenates of the common metals with a solution of ferric chloride. The arsenates of lead and mercurous mercury gave sols and white precipitates of the chlorides. On dialysis after filtration these sols gave the characteristic gels of ferric

arsenate. We found, also, that the arsenates of other metals gave the same gels containing none of the metal whose arsenate was used. This was true of arsenates of all the common metals except stannic tin and the soluble arsenates of the alkali group. Dialysis removed all the soluble products of the reaction, thus disturbing the equilibrium and leaving the insoluble ferric arsenate in the highly hydrated gel form. Ferrous arsenate dissolved in a solution of ferric chloride gave, on dialysis, an excellent red gel which contained both ferrous and ferric iron. In most cases these gels formed when nearly all the chloride ion was gone but there were a few instances where considerable remained. This then dialyzed out very slowly.

A sample of ferric arsenate in a solution of chromium chloride on dialysis gave a good green gel which contained only a trace of iron. This shows that in the relation of chromium to iron, at least, it is a matter of mass action, depending on which salt is in excess to determine whether we get the arsenate of iron or of chromium in the gel form.

Two samples of cadmium arsenate in ferric chloride solution were dialyzed. One gave an excellent red gel in about three weeks; the other in a few days gave a yellowish butter. This contracted but little and took three months to dialyze out all the chloride ions. At the end of that time it was more nearly a gel in texture but was still quite buttery and light yellow in color. This same difference was observed with two samples of lead arsenate in ferric chloride solution. The probable explanation is that we get the quickly formed butter when there is not enough excess ferric chloride solution, and on dialysis this slight excess is removed too suddenly for the change to gel form to take place. This is substantiated by the fact that some of the butter from the lead arsenate was redissolved in a large excess of ferric chloride solution and gave, on dialysis, a splendid red gel. The behavior of the mixture of solutions of ferric chloride and arsenic acid greatly strengthens this view.

After this work on gels had been completed we found that E. A. Schneider<sup>1</sup> had already done a small amount of work along the same line. He had dialyzed the sol of calcium phosphate in ferric chloride solution and had gotten the gel of ferric phosphate as soon as nearly all the chloride ion was removed. He had also observed that this gel dissolved in ammonium hydroxide and on dialysis lost phosphate. This agrees with our observations on this gel and on the original sol of ferric phosphate or arsenate in ammonium hydroxide. He found that if the gel was treated with potassium hydroxide there was a precipitation of ferric hydroxide, while nearly all the phosphate went into solution. We had not tried the addition of the base directly, but found similar results with the ammonia gel or sol when treated with acids and the base added. Schneider sug-

gested this as a method for the separation of iron and phosphorus and extended it to calcium. The calcium phosphate dissolved in ferric sulfate giving a precipitate of calcium sulfate. On addition of potassium hydroxide solution to the filtered sol the iron was precipitated as hydroxide, leaving the phosphate in solution. His aim was to get a method of analysis applicable to humus.

Sodium metaphosphate treated with excess ferric chloride solution gave the characteristic sol and, on dialysis, a good gel of ferric metaphosphate. The pyrophosphate on similar treatment yielded a most excellent deep red gel of ferric pyrophosphate. Ferric hypophosphite gave sols with ferric chloride solution, hydrochloric acid or nitric acid. On dialysis each of these sols yielded a rather poor gel.

**Peptization by Sulfates.**—Aside from any connection with Schneider's work we had already tried using sulfates instead of ferric chloride solution as peptizing agents. On adding to a solution of sodium arsenate an excess of a solution of ferric alum, or of aluminium sulfates, or of chrome alum, the same results were observed as when the chlorides of these metals were used. The sols were apparently very stable. One sample made by treating sodium arsenate with excess of ferric ammonium sulfate solution has stood undialyzed for four months with no sign of settling. On dialysis, however, there is great difference. Inside of a few days a powder begins to form on the walls of the dialyzer and then on the membrane and after a few more days the colloid settles out entirely as a powder. This was found to be the case every time a sulfate was used as a peptizing agent.

**Peptization by Hydrochloric or Nitric Acids.**—The question naturally suggests itself whether the salt (such as ferric chloride) or the acid from hydrolysis does the peptizing. The dialysates from ferric arsenate in ferric chloride solution were acid for ten days. Evidently the way to settle the point was to try hydrochloric acid instead of ferric chloride solution as a peptizing agent. We found that on dialysis of the colorless solution of well washed precipitate in hydrochloric or nitric acid ferric ion diffused through the membrane for about four days. Then a color began to develop and after a few more days a light yellow gel of excellent texture was formed. This gel could be redissolved in acid and the gel obtained again on dialysis or the gel from ferric chloride dissolved in acid and another gel obtained on dialysis. It has been mentioned before that the gel from the ammonium hydroxide peptization could be dissolved in acid and formed again on dialysis. The gel from the pure acid was not so red as the one from ferric chloride solution because, no doubt, of the lack of adsorbed ferric hydroxide. In the case of the ferric chloride peptization the large excess of ferric chloride, the probability that the hydrochloric acid from hydrolysis reacts to dissolve the arsenate, thus

causing more hydrolysis, and the fact that so much acid dialyzes out, led us to expect a very considerable adsorption of ferric hydroxide. Nitric acid may be used instead of hydrochloric but sulfuric acid gives, on dialysis, the powder described under sulfate peptization.

Hydrochloric acid on ferric arsenate probably forms ferric chloride and arsenic acid, or an acid ferric arsenate. The solution thus formed passes from reddish yellow to light yellow to colorless as the acid is added and, on dialysis, this color change reverses. The removal of the hydrochloric acid by dialysis disturbs the equilibrium, reversing the reaction and slowly reforming ferric arsenate, first in the sol and later in the gel condition. We thought it possible to duplicate these results by starting with the substances on the other side of the equilibrium. Arsenic acid was added to ferric chloride solution until the color was nearly gone and the solution dialyzed. In about two weeks there resulted a splendid gel of about the same color as the gel from ferric arsenate in hydrochloric acid. Similar results were obtained using diluted phosphoric acid in ferric chloride solution. If too concentrated solutions were used a powder and then a butter was obtained. This confirms our conclusions about the butter as given above.

**Peptization of Other Salts by Ammonium Hydroxide.**—The pyrophosphate of ferric iron peptized readily in ferric chloride solution forming a red sol. After two months' dialysis an excellent compact deep red gel resulted. Ferric metaphosphate was also peptized to a red sol by a little very dilute ammonium hydroxide but was coagulated again by any excess. It yielded no gel on dialysis. Efforts to peptize ferric hypophosphite by ammonium hydroxide failed. Ferric arsenite was readily peptized by ammonium hydroxide to a red-yellow sol. Dialysis did not produce a real gel. Chromium arsenate and phosphate were peptized to a slight extent only by ammonium hydroxide. The same is true of the arsenate of aluminium. The arsenates of zinc and nickel were peptized by this base but on dialysis these colloids were precipitated.

**Sols and Gels of Aluminium and Chromium Salts.**—When a solution of aluminium chloride was added in excess to sodium arsenate solution the precipitate first formed was redissolved and, on dialysis, a colorless gel formed on the dialyzer. This gel seemed to retard the diffusion of ions, for when there was about one-fourth inch of gel on the membrane the dialysates showed almost no chloride ions while the sol above the gel was rich in chlorides. On changing this sol to another dialyzer a gel formed. However, the disturbance at the time of transfer caused the gel to be lumpy. We tried one sample with which we shook the dialyzer every day to keep the sol uniform. The gel developed from top to bottom but in lumps. The aluminium arsenate gels were not nearly as good as those of iron. With chromium arsenate the results were very like those

with aluminium. The gels were perhaps a little better and of greenish color.

### Summary.

1. The precipitated arsenates and phosphates of ferric iron are rather gelatinous and difficult to wash free from adsorbed ions. However, they may be purified by repeated shaking with sand and a large amount of water followed by decantation or filtration.

2. Ferric orthoarsenate and orthophosphate may be peptized by comparatively small amounts of ammonium hydroxide, yielding stable colloids. On long-continued dialysis these were found, contrary to the experience of Grimaux, to form excellent deep red gels. The composition of both sol and gel of the arsenate correspond closely to the formula  $\text{FeAsO}_4 \cdot \text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ . The change in composition from that of the precipitated arsenate and the formation of the final sol and gel are brought about by the removal of ammonium arsenate during dialysis. The same is true of the phosphate.

3. The peptization mentioned in (2) is probably due to the action of the hydroxyl ion since, with limitations, other hydroxides may be substituted for ammonium hydroxide and substituted ammonias may be used as peptizing agents. The colloid formed by using a water solution of methyl amine yielded, on continued dialysis, a splendid gel of a deeper red color than the others.

4. Either colloid has great adsorptive power, carrying into suspension with it other insoluble hydroxides at the time of its peptization. This power, however, is greatly lessened by the removal of arsenate during dialysis.

5. Ammonium hydroxide also peptizes ferric pyrophosphate, ferric metaphosphate and ferric arsenite. With arsenates and phosphates of chromium and aluminium there seems to be very little peptization. With the arsenates and phosphates of zinc and nickel unstable sols are formed, settling out on dialysis.

6. Ferric orthoarsenate or orthophosphate is peptized by ferric chloride solution as found by Grimaux and yields, on dialysis, an excellent red gel after removal of most of the chloride ion. In similar manner the orthoarsenate or orthophosphate of chromium or aluminium are peptized by solutions of chromium chloride or aluminium chloride and form gels on dialysis.

7. The precipitated orthoarsenates or orthophosphates of any of the common metals are peptized in ferric chloride solution and yield, on dialysis, gels of ferric arsenate or phosphate. If the ferric chloride solution is overloaded with the arsenate or phosphate, a butter is formed which is very slow to give up its adsorbed ions.

8. If a solution of a sulfate is used as the peptizing agent, instead of a

chloride as mentioned in (6), a sol is formed stable on standing but forming a powdery sediment on dialysis and completely settling out.

9. In all examples of peptization by salts as mentioned in (6), (7) and (8) the action is due to acid hydrolysis, as shown by the fact that hydrochloric or nitric acid may be used as peptizing agents with equally good results. The sols formed by acids give excellent gels on dialysis but lighter in color than those formed from ferric chloride solution. If sulfuric acid is used the results are those observed in the use of any sulfate as the peptizing agent. There are at least two kinds of peptization of these arsenates and phosphates, that by acids and that by bases.

10. The formation of the sol and gel in the case of the acid peptizations is due to the disturbance of the equilibrium by dialysis. This is shown by the fact that good gels may be formed by dialyzing dilute mixtures of ferric chloride solution and arsenic or phosphoric acid, the phosphoric acid giving a gel excellent in clearness as well as in texture.

11. The metaphosphate, pyrophosphate and hypophosphite of ferric iron behave like the orthophosphate in peptization by acids and ferric chloride. Ferric pyrophosphate in ferric chloride solution formed a splendid deep red gel on dialysis.

OBERLIN, OHIO.

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## THEORY OF COLLOIDS.

BY JOHN ARTHUR WILSON.

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The object of the present paper is the promulgation of further reasoning in favor of the "complex" theory of colloid formation and the elucidation of the very interesting and important conclusions which follow. The fundamental assumption of this theory is that the colloidal state in sols owes its stability to the formation of a complex between the particles of the disperse phase and certain substances present or formed in the dispersion medium during the preparation of the colloid. The sols of the noble metals have been cited as an argument against this theory, but Beans and Eastlack<sup>1</sup> have shown that the presence of chloride, bromide, iodide, or hydroxide ions in concentrations from 0.00005 *N* to 0.005 *N* has a marked stabilizing effect on gold sols and that the colloid particles become negatively charged. In concluding, these authors consider that the electrical synthesis of colloids consists of a thermo-mechanical dispersion of the metal, followed by the formation of a colloidal complex between the dispersed metal and certain ions present in the medium.

The assumption of the formation of such a complex between any colloid particles and electrolytes present in the dispersion medium is not unreasonable. Carbon is a typical *adsorbing* agent and happily one, the stability of whose compounds has been extensively investigated. The

<sup>1</sup> THIS JOURNAL, 37, 2667-83 (1915).

data leading to the formulation of Baeyer's Strain Theory indicates that the four valencies of the carbon atom are directed toward the vertices of a regular tetrahedron, of which the carbon atom is the center. This being true, any atom *within* a given particle of carbon will attract and be attracted by the atoms immediately surrounding it, but one at the surface is attracted only towards atoms of the particle and consequently has one or more of its valencies directed away from the particle, and therefore unsatisfied. In a lump of carbon this free or residual valency might be relatively insignificant but would increase to huge proportions as the carbon became more and more highly dispersed. It is probable that every substance possesses a certain amount of residual valency at its surface, which tends to cause it to combine with substances approaching its surface. As in chemical combination in general, such combination is probably selective. Indeed, Beans and Eastlack (*Loc. cit.*) have shown that the presence of fluoride ions does not stabilize gold sols, while Lenher<sup>1</sup> has shown that gold fluoride is incapable of existence, not only in the presence of water, but under ordinary laboratory conditions.

Apparently the colloid particle takes its electrical charge from the ions with which it combines, or in some cases, acquires a charge by ionizing itself. Such a charge seems to be necessary to the stability of the colloid state in sols, which is explained to some extent by the fact that particles with like charges tend to repel each other, thus preventing coalescence.

Associated with any charged particle there will be a number of ions of opposite charge, which cannot be separated from the surface of the particle, excepting by very small distances, or by being replaced by other ions of the same sign, which means that the distribution of ions in the layer of solution surrounding the particle will be different from that in the bulk of the dispersion medium, a condition to which Donnan's<sup>2</sup> work on membrane equilibria can be applied. Donnan considers an aqueous solution of a salt, NaR, such as Congo red, in contact with a membrane which is impermeable to the anion R' and the nonionized salt, but will allow Na<sup>+</sup> or any other ion to pass freely through it. On the other side is an aqueous solution of sodium chloride, which will diffuse from its Solution II into the Solution I of NaR. When equilibrium is established, if a small virtual change is made reversibly at constant temperature and volume, the free energy will remain unchanged, *i. e.*, no work will be done. The change here considered is the transfer of  $\delta n$  moles of Na<sup>+</sup> and Cl' from II to I. The work which equals zero is

$$\delta n RT \log \frac{[\text{Na}^+]_{\text{II}}}{[\text{Na}^+]_{\text{I}}} + \delta n RT \log \frac{[\text{Cl}^-]_{\text{II}}}{[\text{Cl}^-]_{\text{I}}} = 0$$

or

<sup>1</sup> THIS JOURNAL, 25, 1136 (1903).

<sup>2</sup> Z. *Electrochemie*, 17, 572 (1911).

$$[\text{Na}^+]_{\text{II}} \times [\text{Cl}^-]_{\text{II}} = [\text{Na}^+]_{\text{I}} \times [\text{Cl}^-]_{\text{I}}.$$

By a continuation of this reasoning it can be shown that whatever diffusible binary electrolytes be added to Solution II, when equilibrium is established, the *products* of concentrations of any pair of diffusible and oppositely-charged ions will be equal in the two solutions.

If a substance is dispersed to the colloid state in a solution of the electrolyte MN and combines with a portion of  $\text{M}^+$  (not necessarily in equivalent quantity from a chemical standpoint), then at the surface of the colloid particles there will be a certain concentration of  $\text{N}'$  bound by electrochemical attractions to the colloid. This surface layer of solution will also contain  $\text{M}^+$  and  $\text{N}^-$  and will thus bear the same relation to the bulk of solution as did Solution I to Solution II in Donnan's work just quoted, and consequently the product  $[\text{M}^+] \times [\text{N}^-]$  will be equal in the surface layer and bulk of solution, and since the concentrations of  $\text{M}^+$  and  $\text{N}^-$  are *unequal* in the surface layer and *equal* in the bulk of solution, *the total concentration of ions will be greater in the former than in the latter.*

In the bulk of solution let  $x$  = concentration of positive or negative ions.

In the surface layer surrounding particle let  $y$  = concentration of ions of same sign as charge on the colloid particle.

$z$  = concentration of ions bound to the colloid by electrochemical attractions.

Therefore  $y + z$  = concentration of ions of opposite sign to that on the colloid particle.

Let  $e$  = excess of concentration of diffusible ions of the surface layer over that of the bulk of solution.

In order to keep the reasoning as simple as possible only binary electrolytes will be considered, although it will be obvious that the reasoning can be extended to include ions of any valency. From the law of "equality of products" just discussed

$$x^2 = y(y + z)$$

and since

$$\begin{aligned} 2x + e &= 2y + z \\ z &= \sqrt{4ex + e^2}. \end{aligned}$$

If unit quantity of colloid and unit volume are considered,  $z$  represents the quantity of electrolyte combined with the colloid. But the generally accepted empirical formula for adsorption (using the same system of notation) is

$$z = kx^{1/p}$$

where  $p$  represents a constant, usually about 2, so that generally

$$z = k\sqrt{x}.$$

The similarity of the equations is striking and in certain cases, and



within limits, they would give similar curves, but they are not identical, and here it should be noted that the latter formula is at best only empirical, while the former follows from well-founded assumptions.

The different distribution of ions in the surface layer and bulk of solution will result in a difference of potential, the formula for which is given by Donnan<sup>1</sup> as follows:

$$E = \frac{RT}{F} \log \frac{1}{\lambda}$$

Or, in the notation adopted in this paper,

$$E = \frac{RT}{F} \log \frac{x}{y} = \frac{RT}{F} \log \frac{2x}{-z + \sqrt{4x^2 + z^2}}$$

But  $z$  has a limiting maximum value, since the amount of electrolyte which can combine with a colloid of definite degree of dispersion is limited by the amount of residual valency at the surface, or, in the case of an ionizing colloid, the portion ionized cannot exceed the whole. Hence,

$$\lim_{x \rightarrow \infty} E = \frac{RT}{F} \log \frac{2x}{\sqrt{4x^2}} = 0,$$

proving that the difference of potential existing between the surface layer surrounding the colloid particle and the bulk of solution will diminish as the concentration of electrolyte is increased, after the combination of colloid and electrolyte has reached or neared its maximum. When this difference of potential has become sufficiently small a condition is established which is favorable to the coalescence of the particles. Assuming that a given potential difference is required for the maintenance of the colloid state in sols, the amount of electrolyte required for precipitation of the colloid will depend upon the maximum value for  $z$ . In the case of suspensoids this is probably very small, while for many emulsoids it is known to be comparatively high.

Where a charged particle combines directly with an ion of opposite sign, precipitation must follow. The cause of the co-precipitation of oppositely-charged colloids is equally obvious, but it might be well to point out in passing that the rate of this precipitation might be controlled by suitable regulation of the concentration of electrolytes in the dispersion medium. Similar lines of reasoning explaining the swelling and contracting action of electrolytes upon colloid jellies have been worked out by H. R. Procter and the author and appear elsewhere.<sup>2</sup> Whatever herein expressed may seem opposed to the generally-accepted views on colloids can be tested as the formulas derived are quantitative in character. The author expresses the hope that they may lead a step nearer to the goal of colloid chemists.

MILWAUKEE, WIS.

<sup>1</sup> *Loc. cit.*

<sup>2</sup> *J. Chem. Soc.*, 109, 307 (1916); *J. Am. Leather Chem. Assoc.*, 11, 8 (1916).

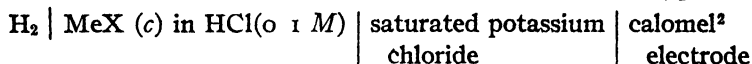
[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF THE UNIVERSITY OF PENNSYLVANIA.]

# THE HYDROGEN AND CHLORINE ION ACTIVITIES OF SOLUTIONS OF POTASSIUM CHLORIDE IN 0.1 MOLAL HYDROCHLORIC ACID.

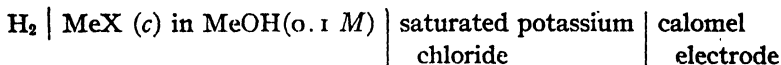
By HERBERT S. HARNED.

Received July 1, 1916.

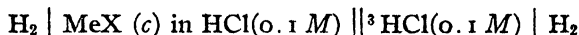
In a recent communication,<sup>1</sup> measurements of cells of the type



and



showed that the hydrogen ion activity of the acid and the hydroxyl ion activity of the base were increased by the addition of neutral salts. Further, the evidence obtained with the acid and salt solutions showed that the increase in hydrogen ion activity on the addition of salts differed little, if at all, for the different salts used. At that time a plot was predicted which was thought to give the change in electromotive force of the hydrogen electrode with the change of salt concentration in the acid. Such a change in electromotive force is obviously equal to the electromotive forces of the cells



at different salt concentrations (*c*). From these, if the hydrogen ion activity of the acid is known, the hydrogen ion activity of the acid-salt solutions can be computed.

The most important difficulty previously encountered in obtaining the electromotive forces of the cells



consisted in the elimination of the liquid potentials set up between the saturated potassium chloride solution and the solutions of the salt in the acid. Saturated potassium chloride, many times recommended for the elimination of liquid potentials, was shown to give different potentials against solutions of different concentrations of the same salt, and against the same concentrations of different salts. A similar series of measurements had been made by Poma<sup>4</sup> who used a saturated ammonium nitrate solution for the elimination of the liquid potentials. If Poma's results are compared with those mentioned above, it is clear that the liquid

<sup>1</sup> THIS JOURNAL, 37, 2460 (1915).

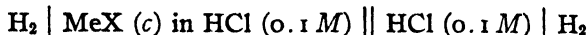
<sup>2</sup> This symbolizes a series of cells containing salt at a series of concentrations (*c*).

<sup>3</sup> The double bar means that the liquid potential has been eliminated.

<sup>4</sup> *Z. physik. Chem.*, 87, 197 (1914); 88, 671 (1914).

potentials produced between the solutions of the salts in the acid and the ammonium nitrate solution are greater than those produced when potassium chloride is used. The important point is that neither potassium chloride or ammonium nitrate eliminates these liquid potentials.

For this reason it is desirable to determine the electromotive forces of the cells



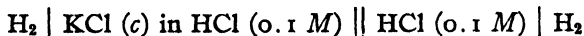
by the use of a method which is free from these liquid potential difficulties. In this paper such a procedure has been adopted.

#### The Method of this Communication.

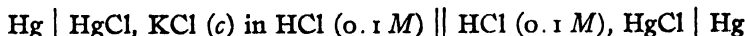
If potassium chloride be added to the hydrochloric acid in the cell



a change in electromotive force will occur. The total effect will be due to the sum of the variations of the two electrodes. Any change in the hydrogen ion activity or the chlorine ion activity will be registered at the hydrogen electrode and the calomel electrode, respectively. This total change in electromotive force will be equal to the sum of the changes in electromotive forces of the cells

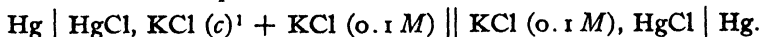


and



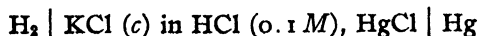
when the concentration of the potassium chloride is the same.

If the ion activities of 0.1 *M* potassium chloride and 0.1 *M* hydrochloric acid are the same, then the electromotive forces of the last series of these cells would equal the electromotive forces of the cells



In this communication the following procedure has been adopted:

(1) The electromotive forces of the cells



have been measured. From these, the drops in electromotive forces of the cell



on the addition of potassium chloride of different concentrations to the acid have been computed. The electromotive forces of the cells



have then been calculated by subtracting the electromotive forces of the cells



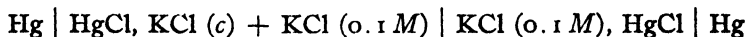
<sup>1</sup> Thus, as will be seen later, a concentration of 0.06 *M* salt in 0.1 *M* hydrochloric acid is compared with 0.16 *M* salt.

obtained from the plot X of the earlier communication from the drops in electromotive forces of the cell

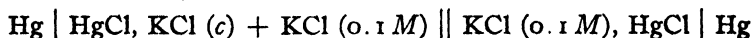


on the addition of potassium chloride.

(2) The electromotive forces of the cells

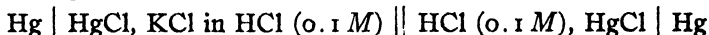


have been measured, and from these the electromotive forces of the cells

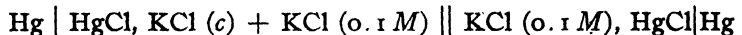


have been obtained by eliminating the liquid potential by means of a suitable formula.

(3) Having obtained the electromotive forces of the cells



and



by the above methods, we are in a position to test the contentions made in the previous article. The last part of this paper will contain a discussion of the values thus obtained and the calculation of the hydrogen and chlorine ion activities of the acid-salt solutions from these values.

### Measurements.

1. Cells,  $\text{H}_2 \mid \text{KCl (c) in HCl (0.1 M), HgCl} \mid \text{Hg}$ .—A cell in the form of an H-tube was used, one limb of which contained the calomel electrode, the other the hydrogen electrode. Precautions were taken to separate thoroughly the two limbs of the apparatus, and in no case here recorded did the hydrogen electrode take on a gray coating of mercury. Carefully purified chemicals were employed. Before making up the cell, the calomel paste was washed by decantation six or seven

TABLE I.

Mols salt per l.		Barometric pressure.	E. M. F. (obs.).	Correction for pressure of $\text{H}_2$ .	Corrected E. M. F.
0.000	No. 1	769.0	0.39915	0.00022	0.39937
0.000	No. 2	765.0	0.39905	0.00029	0.39934
0.060	No. 3	764.5	0.38881	0.00030	0.38911
0.060	No. 4	767.0	0.38889	0.00026	0.38915
0.100		759.5	0.38370	0.00040	0.38410
0.120		765.0	0.38112	0.00029	0.38141
0.200		763.0	0.37439	0.00033	0.37472
0.240		758.0	0.37100	0.00042	0.37142
0.400		764.0	0.36231	0.00031	0.36262
0.600		765.0	0.35360	0.00029	0.35389
0.900		765.0	0.34404	0.00029	0.34433
1.200		765.0	0.33602	0.00029	0.33631
1.800		765.0	0.32268	0.00029	0.32297
2.400		764.5	0.31110	0.00030	0.31140
3.000		765.0	0.30021	0.00029	0.30050

times with the solution to be introduced in the cell and the mixture was allowed to stand three days at 25° before being used. Finally, the cells were kept in a thermostat for a period of two to four days until further shaking of the calomel electrode caused a variation of less than 0.05 of a millivolt over a period of twenty-four hours. All measurements were carried out at 25° with a maximum variation of 0.03°.

Table I shows the values obtained.

The correction of the pressure of the hydrogen was computed by the formula  $(RT/2F) \ln 1/p$  as in the previous communication. The corrected electromotive force is what the electromotive force of the cell would be if the pressure of the hydrogen in the cell was one atmosphere<sup>1</sup> at 25°. No. 1 and No. 2 are two completely different cells. No. 3 and No. 4 represent readings taken at the beginning and the end of a twenty-four hour run.

2. Cells,  $\text{Hg} \mid \text{HgCl}, \text{KCl} (c) + \text{KCl} (0.1 M) \mid \text{KCl} (0.1 M), \text{HgCl} \mid \text{Hg}$ .—It will not be necessary to go into detail in describing these measurements. Let it suffice to say that, if the solutions used in the calomel electrodes in these cells were allowed to stand three or four days at 25° before being introduced, measurements of the cells could be reproduced to within 0.05 of a millivolt. The object of these measurements is to determine the electromotive forces of the cells



Hence, it is necessary to eliminate the liquid potential from the cells in which ion-transference is taking place. To this end a formula, derived by MacInnes<sup>2</sup> from thermodynamic considerations of the electromotive forces of cells with and without transference, was used. This formula must hold throughout all ranges of concentration. It is

$$E_l = E_t (1 - 1/2n_c)$$

where  $E_l$  is the liquid potential,  $E_t$  the total electromotive force of the cell, and  $n_c$  the cation transference number. The equation of MacInnes gives the same results as would be obtained from the Nernst formula

$$E_l = (n_c - n_a)RT \ln c_1/c_2$$

if the correct activity values for the ions be substituted for the concentrations. Accurate data for the cation transference number of potassium chloride above 0.2 *M* were not available. The value<sup>3</sup> 0.495 was used throughout the complete range of concentrations employed.

These results are compiled in Table II.  $E_t$  is the electromotive forces of the cells with transference,  $E_l$  the liquid potential, and  $E_t + E_l$  the electromotive forces of the cells after the liquid potential has been elim-

<sup>1</sup> See Lewis and Randall, *THIS JOURNAL*, 36, 1973 (1914).

<sup>2</sup> MacInnes, *THIS JOURNAL*, 37, 2301 (1915).

<sup>3</sup> Noyes and Falk, *THIS JOURNAL*, 33, 1336 (1911).

inated. Finally, the chlorine ion activities of the potassium chloride solutions have been calculated on the basis that the chlorine ion activity of 0.1 *M* potassium chloride is 0.0730. (This will be referred to later.)

TABLE II.

Conc. of salt ( <i>c</i> + 0.1 <i>M</i> ).	$E_t$ .	$E_t$ .	$E_t + E_i$ .	Activity of the chlorine ion.
0.100	0.00000	0.00000	0.00000	0.0730
0.160	-0.01044	-0.00011	-0.01055	0.1101
0.200	-0.01536	-0.00016	-0.01552	0.1336
0.220	-0.01802	-0.00018	-0.01820	0.1483
0.300	-0.02475	-0.00025	-0.02500	0.1932
0.340	-0.02785	-0.00028	-0.02813	0.2183
0.500	-0.03637	-0.00037	-0.03674	0.3051
0.700	-0.04443	-0.00045	-0.04488	0.4191
1.000	-0.05287	-0.00053	-0.05340	0.5836
1.300	-0.05910	-0.00059	-0.05969	0.7455
1.900	-0.06843	-0.00069	-0.06912	1.0760
2.500	-0.07572	-0.00076	-0.07648	1.4332
3.100	-0.08165	-0.00082	-0.08247	1.8097

### 3. Comparison of the Cells.—

$\text{Hg} | \text{HgCl}, \text{KCl} (c) + \text{KCl} (0.1 \text{ } M) || \text{KCl} (0.1 \text{ } M), \text{HgCl} | \text{Hg}$   
and

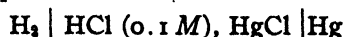
$\text{Hg} | \text{HgCl}, \text{KCl} (c) + \text{HCl} (0.1 \text{ } M) || \text{HCl} (0.1 \text{ } M), \text{HgCl} | \text{Hg}.$

The comparison of the above cells can best be understood from Table III.

TABLE III.

Conc. of salt <sup>1</sup> ( <i>c</i> ).	(1).	(2).	(3).	(4).
0.060	-0.01022	-0.00010	-0.01012	-0.01055
0.100	-0.01525	-0.00015	-0.01510	-0.01552
0.120	-0.01794	-0.00020	-0.01774	-0.01820
0.200	-0.02463	-0.00030	-0.02433	-0.02500
0.240	-0.02793	-0.00040	-0.02753	-0.02813
0.400	-0.03673	-0.00075	-0.03598	-0.03674
0.600	-0.04546	-0.00125	-0.04421	-0.04488
0.900	-0.05502	-0.00225	-0.05277	-0.05340
1.200	-0.06304	-0.00375	-0.05929	-0.05969
1.800	-0.07638	-0.00775	-0.06863	-0.06912
2.400	-0.08795	-0.01200	-0.07595	-0.07648
3.000	-0.09885	-0.01640	-0.08245	-0.08247

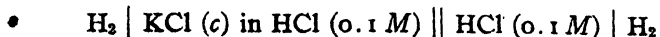
Col. 1 gives the drop in electromotive force of the cell



on the addition of potassium chloride at a concentration of *c* mols per liter.

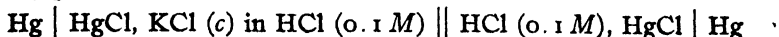
Col. 2 gives the electromotive forces of the cells

<sup>1</sup> Thus, a concentration of 0.06 *M* salt in 0.1 *M* hydrochloric acid is compared with a concentration of 0.16 *M* salt.



as obtained from the plot X of the previous communication.

Col. 3 gives the electromotive forces of the cells



obtained by subtracting the values in Col. 2 from those in Col. 1.

Col. 4 gives the electromotive forces of the cells

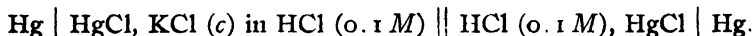


obtained from  $E_i + E_i$  in Table II.

Now, as has been stated under the discussion of the general method here employed, if the activity of the chlorine ion in 0.1 *M* hydrochloric acid is equal to the activity of the chlorine ion in 0.1 *M* potassium chloride, then the values for the cells in Cols. 3 and 4 should be identical. As can readily be seen, there is a striking agreement between the values obtained even up to a salt concentration of 3 *M*. The widest deviation between the two series of results is 0.00076 volt at a salt concentration of 0.400 *M*. Furthermore, it is to be noticed that at every concentration of salt, the electromotive force of the cell

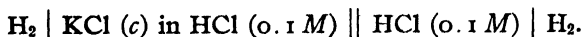


is greater than that of the cell

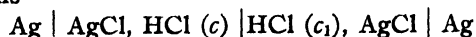


This deviation may be due to two causes; firstly, the X-plot of the previous communication may be faulty; secondly, the ion-activity of the hydrochloric acid may be greater than the ion activity of the potassium chloride at 0.1 *M* concentration. Since the widest deviations occur in the more dilute solutions and since the values in Col. 4 are in every case greater than those in Col. 3, there is great likelihood that the ion activity of the acid is greater than that of the salt.

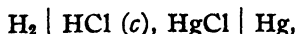
**4. Further Discussion of the Results. Final Calculation of the Electromotive Forces of the Cells.—**



There is as yet no reliable value for the activity of the hydrogen and chlorine ions in 0.1 *M* hydrochloric acid. From the data obtained by Jahn<sup>1</sup> on the cells



and by Ellis<sup>2</sup> on the cells



the latter has calculated the activity coefficient<sup>3</sup> of 0.1 *M* hydrochloric acid. In this calculation, the assumption was made that at an acid con-

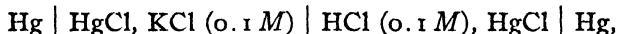
<sup>1</sup> *Z. physik. Chem.*, 33, 545 (1900).

<sup>2</sup> *THIS JOURNAL*, 38, 737 (1916).

<sup>3</sup> The activity coefficient is equal to the activity divided by the concentration.

centration of 0.00167, the activity coefficient equalled the conductance viscosity ratio. Ellis obtained in this manner the value 0.843 for the activity coefficient, which makes the hydrogen ion activity 0.0843. More reliable calculations have been made by Ellis on the activity coefficient of 0.1 *M* potassium chloride from the osmotic pressure calculations of Bates<sup>1</sup> and the electromotive force measurements of MacInnes and Parker.<sup>2</sup> The values 0.732 and 0.727 for the activity coefficients are obtained from these two sources. If we take the ion-activity of 0.1 *M* potassium chloride to be 0.0730, then there is reason to believe that the ion-activity of 0.1 *M* hydrochloric acid is less than 0.0843. Ellis was aware of the provisional nature of this value.

According to the formula of Lewis and Sargent,<sup>3</sup> the liquid potential at the surface of a 0.1 *M* potassium chloride solution and a 0.1 *M* hydrochloric acid solution is -0.0284. Recent measurements of the cell



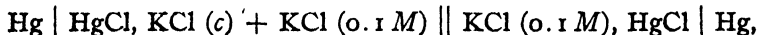
obtained by Lewis and Sebastian,<sup>4</sup> give the value -0.0284. This argues that there is little, if any, difference between the ion activities of the acid and the salt at this concentration.

From the results reported in this paper, it is thought that the activity of the ions in 0.1 *M* hydrochloric acid is greater than in 0.1 *M* potassium chloride but only slightly greater. If 0.0730 be accepted to represent the ion-activity of the salt, there is reason to assume that the ion-activity of the acid is 0.0755. The arbitrary nature of this choice is realized; it simply fits in with the large amount of evidence obtained by the author.

The extent of this correction can best be shown by Table IV and the plots in Fig. 1. Table IV contains the following:

(1) Salt concentration (*c*).

(2) The values of Col. A were obtained on the assumption that the ion activities of 0.1 *M* hydrochloric acid equalled the ion activities of 0.1 *M* potassium chloride. In other words, the electromotive forces of the cells



(*E*<sub>t</sub> + *E*<sub>h</sub>, Table II) were subtracted from the drop in electromotive forces of the cell



on the addition of potassium chloride (Col. 2, Table III). A in Fig. 1 is the plot of these values. Here, the electromotive forces are plotted against the salt concentration (*c*) in gram equivalents per liter.

<sup>1</sup> THIS JOURNAL, 37, 1421 (1915).

<sup>2</sup> *Ibid.*, 37, 1445 (1915).

<sup>3</sup> *Ibid.*, 31, 363 (1909).

<sup>4</sup> Lewis and Randall, *Ibid.*, 36, 1973 (1914).



(3) The column headed "dotted line" and corresponding to the dotted line in Fig. 1 was obtained as follows:

a. It was assumed that the ion-activity of the acid was 0.0755 and the salt 0.0730.

b. The chlorine ion-activities of the acid-salt mixtures were assumed to be equal to those of the salt solution plus 0.0025 at the different concentrations. This should be a good approximation.

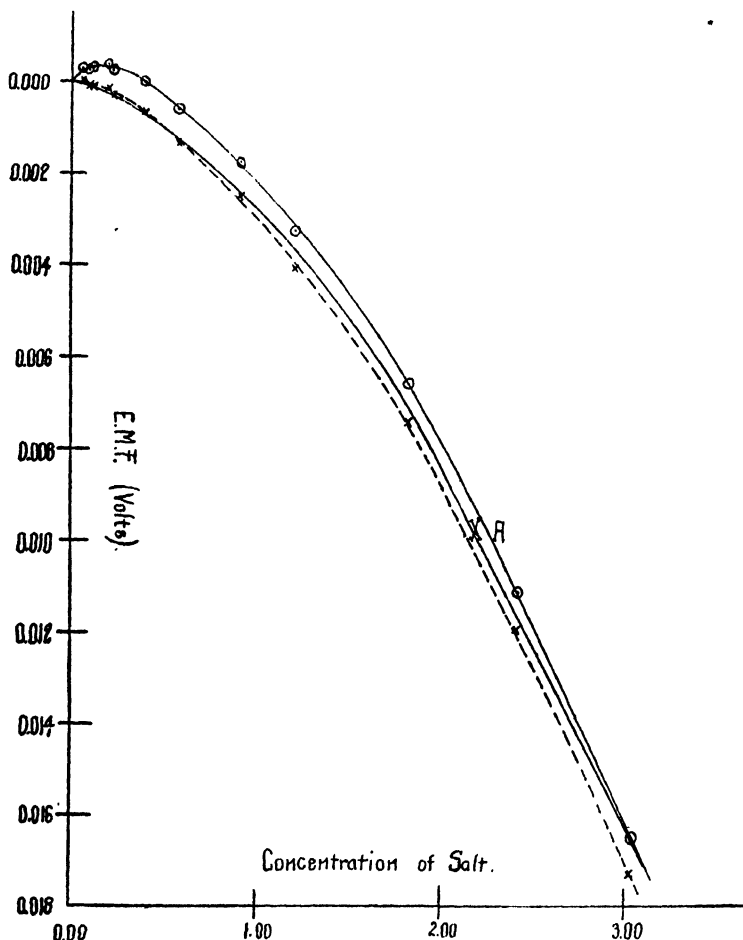


Fig. 1.

c. From this data, the electromotive forces of the cells

$\text{Hg} \mid \text{HgCl}, \text{KCl in HCl (0.1 M)} \parallel \text{HCl (0.1 M)}, \text{HgCl} \mid \text{Hg}$   
 were calculated. By subtracting these values from the drops in electro-  
 motive force of the cell



on the addition of potassium chloride of concentration ( $c$ ), the electromotive forces of the cells



are obtained. This gives the final data on the electromotive forces of the last of these cells as obtained from the measurements in this paper.

(4) The Col. X, corresponding to X in Fig. 1, represents the electromotive forces of this last series of cells as obtained from the Plot X of the earlier communication.

(5) The last column represents the difference between the values under "dotted line" and X.

TABLE IV.

Conc. of salt ( $c$ ).	A.	Dotted line.	X.	Difference.
0.060	0.00033	0.00002	-0.00010	0.00012
0.100	0.00027	-0.00011	-0.00015	0.00004
0.120	0.00026	-0.00017	-0.00020	0.00003
0.200	0.00037	-0.00017	-0.00030	0.00013
0.240	0.00020	-0.00038	-0.00040	0.00002
0.400	0.00001	-0.00065	-0.00075	0.00010
0.600	-0.00058	-0.00128	-0.00125	-0.00003
0.900	-0.00162	-0.00236	-0.00225	-0.00011
1.200	-0.00335	-0.00413	-0.00375	-0.00038
1.800	-0.00726	-0.00808	-0.00775	-0.00033
2.400	-0.01147	-0.01230	-0.01200	-0.00030
3.000	-0.01638	-0.01721	-0.01640	-0.00081

A very close agreement is obtained except at the higher concentrations of salt. In no case is the difference more than 1 millivolt. This may be due to an error in the values obtained in the previous communication. The large increase in the hydrogen ion activity in the more concentrated solutions would tend to diminish the liquid potential between the acid-salt solutions and the solution of saturated potassium chloride there used. This effect would act in such a way as to increase the electromotive force of the cell and thus render the electromotive force decrease of the Plot X too small. We cannot at present be entirely certain of this, for at these high concentrations an error may have been introduced in assuming that the cation transference number of potassium chloride is 0.495 throughout the complete range of concentrations. The evidence offered in this paper would tend to prove that this value varies slightly, if at all. However, if the cation transference number decreases with increasing salt concentration, there will result a smaller difference between the Plot X and the dotted line.

5. The Ion Activities of Solutions of Potassium Chloride in 0.1 M Hydrochloric Acid.—Table V gives these ion activities calculated from the data thus obtained. The hydrogen ion activities are calculated from the electromotive forces in Table IV. Up to a concentration of

0.600 *M* salt, these have been obtained from the values given in Col. X; at salt concentrations higher than this, they have been obtained from the means of the values of Col. X and Col. "dotted line." The chlorine ion activities have been obtained by adding 0.0025 to the values given in Table II. The last column gives the free energy transfer of one gram ion of hydrogen from a solution of 0.1 *M* hydrochloric acid to a solution of 0.1 *M* hydrochloric acid containing potassium chloride at the concentration designated.

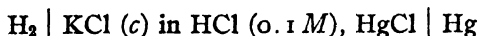
TABLE V.

Conc. of salt ( <i>c</i> ).	Hydrogen ion activities.	Chlorine ion activities.	Free energy transfer.
0.000	0.0755	0.0755	...
0.060	0.0758	0.1126	-9.65
0.100	0.0759	0.1361	-14.47
0.120	0.0761	0.1508	-19.30
0.200	0.0765	0.1957	-28.95
0.240	0.0767	0.2208	-38.60
0.400	0.0777	0.3076	-72.37
0.600	0.0793	0.4216	-120.6
0.900	0.0826	0.5861	-222.0
1.200	0.0880	0.7480	-382.0
1.800	0.1027	1.0785	-763.3
2.400	0.1211	1.4357	-1172.0
3.000	0.1452	1.8122	-1621.0

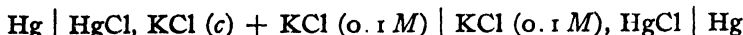
Since an error of 0.00025 volt corresponds to an error of 1% in the ion activity and since there is still an element of guess-work in the calculation of these values, an accuracy of less than 1% is not claimed.

### Summary.

#### 1. Measurements of the cells



and



up to a concentration of 3 *M* potassium chloride have been made.

2. From these, if the ion activities of 0.1 *M* potassium chloride and 0.1 *M* hydrochloric acid are known, the electromotive forces of the cells



can be calculated.

3. The measurements here recorded, along with those of an earlier communication, indicate that if the ion activity of 0.1 *M* potassium chloride is 0.0730, then the ion activity of 0.1 *M* hydrochloric acid is 0.0755.

4. From these two values, and the measurements of the above cells, the hydrogen and chlorine ion activities of solutions of potassium chloride at different concentrations in 0.1 *M* hydrochloric acid have been computed.

[CONTRIBUTION FROM THE CHEMICAL SECTION, IOWA AGRICULTURAL EXPERIMENT STATION.]

## ESTIMATION OF CALCIUM IN ASH OF FORAGE PLANTS AND ANIMAL CARCASSES.

By S. B. KUZIRIAN.

Received June 24, 1916.

An accurate as well as a rapid method for the estimation of calcium in forage plants and animal carcasses in agricultural experiment stations is of prime importance in studying the relationship between the growing plant or animal on the one hand and the soil or food supply on the other.

Having had occasion in this laboratory to make a large number of calcium determinations on samples of forage plants and animal carcasses, the disadvantages and inconveniences of the methods in common use soon became apparent. In the course of these analyses the method described in this paper was found to be superior both in regard to accuracy and convenience.

Thompson and Morgan<sup>1</sup> attempt the precipitation of calcium as oxalate in the presence of large excess of phosphoric acid in acetic acid solution. McCrudden<sup>2</sup> likewise tries to estimate the calcium without first removing the phosphoric acid.

The separation of phosphoric acid as mercurous,<sup>3</sup> stannic,<sup>4</sup> bismuthic,<sup>5</sup> silver,<sup>6</sup> etc., phosphates with the subsequent removal of these precipitants by some suitable analytical operations is too tedious, requiring prolonged time for execution. These methods are, therefore, out of consideration for general use in experiment stations.

The basic acetic method is the one which has come into most common use, having been adopted as official by the Association of Official Agricultural Chemists. The conditions to be observed with this method are of such a nature, that it is difficult to get concordant results in determinations of manganese, calcium, magnesium and the alkalis. The main objection to this process is the prolonged evaporation which is necessary to reduce a large volume of filtrate into 50 to 75 cc. The action of ammonia salts upon the glass beaker at 80 to 90° is not altogether negligible.

**A More Accurate and Rapid Method.**—Shedd's<sup>7</sup> method, though more convenient and rapid, tends to give higher results due to contamination

<sup>1</sup> *J. Ind. Eng. Chem.*, 3, 398.

<sup>2</sup> *J. Biol. Chem.*, 10, 187.

<sup>3</sup> H. Rose, *Pogg. Ann.*, 76, 218.

<sup>4</sup> W. Reissig, "Zur quantitativen Bestimmung der Phosphorsäure," *Ann. Chem. Pharm.*, 98, 339-344 (1856).

<sup>5</sup> *Compt. rend.*, 50, 416; *Chem. Zentr.*, 1860, 272.

<sup>6</sup> Fresenius' *Quant. Chem. Anal.*, 1, 458.

<sup>7</sup> O. M. Shedd, referee in inorganic plant constituents for the A. O. A. C., *Bur. of Chem., Bull.* 152, 64, 65.

with molybdenum. When, however, the following procedure, which is a slight modification of Shedd's process, is adopted, excellent results are obtained. The modification consists essentially in boiling the calcium oxalate precipitate for 30 minutes on a hot plate, and filtering through a Gooch; then, instead of dissolving this precipitate with hydrochloric acid and reprecipitating with dilute ammonia, which operation seems to be insufficient completely to remove adhering traces of molybdenum,<sup>1</sup> it is ignited to convert the oxalates into oxides, preferably in an electric furnace. It is then dissolved in dilute hydrochloric acid, filtered, some ammonium chloride and ammonia added, and boiled until the odor of ammonia is faint. The precipitated iron and aluminium are removed and the calcium precipitated as oxalate, at this stage of the process, calcium being entirely free from molybdenum salts.<sup>2</sup>

The results shown in Table I were obtained with solutions containing known amounts of calcium and phosphorus. The phosphorus was removed in each case as ammonium phosphomolybdate, according to directions given in the Official Methods<sup>3</sup> (Volumetric Optional) and titrated to make sure that its removal was complete. The estimation of calcium according to the above method was then attempted and the following results were obtained:

TABLE I.—ANALYSIS OF KNOWN SOLUTION FOR CALCIUM AND PHOSPHORUS.

No. of the experiment.	P <sub>2</sub> O <sub>5</sub> taken (as Na <sub>2</sub> HPO <sub>4</sub> ), g.	CaO taken (as Ca(NO <sub>3</sub> ) <sub>2</sub> ), g.	CaO found, g.	Error, g.
1	0.0207	0.0283	0.0283	0.0000
2	0.0207	0.0283	0.0285	+0.0002
3	0.0207	0.0283	0.0283	0.0000
4	0.0207	0.0283	0.0283	0.0000
5	0.0207	0.0283	0.0283	0.0000
6	0.0207	0.0566	0.0566	0.0000
7	0.0207	0.0283	0.0282	-0.0001
8	0.0207	0.0283	0.0283	0.0000

The ease with which closely agreeing duplicates can be obtained when ash of forage plants is analyzed for calcium is shown in Table II. Numbers 1 and 2 in each case are duplicates of the same sample.

<sup>1</sup> On testing qualitatively a series of 8 results obtained according to Shedd's method, all gave indications of molybdenum. The sulfide test was found to be most satisfactory, being sensitive to a small fraction of a milligram of MoO<sub>3</sub>. In all cases calcium oxides were dissolved in hydrochloric acid, made ammoniacal, colorless ammonium sulfide added, digested, filtered and the filtrate made acid with hydrochloric acid. Sometimes a development of a blue coloration on addition of ammonia sulfide indicates a reduced condition of molybdenum.

<sup>2</sup> When two series of eight each were tested for molybdenum similarly, tests were negative in all cases.

<sup>3</sup> Bur. Chem., *Bull.* 107 (1910).

TABLE II.—ANALYSIS OF FORAGE PLANTS<sup>1</sup> FOR CALCIUM.

Lab. No. of sample.	Gram CaO found in aliquots.			% Ca in original sample (according to aliquots).		
	No. 1.	No. 2.	Diff.	No. 1.	No. 2.	Diff.
1072	0.0090	0.0095	0.0005	0.450	0.475	0.025
1073	0.0165	0.0165	0.0000	0.825	0.825	0.000
1074	0.0100	0.0100	0.0000	0.500	0.500	0.000
1075	0.0117	0.0120	0.0003	0.585	0.600	0.015
1076	0.0430	0.0430	0.0000	2.150	2.150	0.000
1077	0.0435	0.0440	0.0005	2.175	2.200	0.025
1079	0.0395	0.0390	0.0005	1.975	1.950	0.025
1086	0.0080	0.0080	0.0000	0.400	0.400	0.000
1089	0.0495	0.0495	0.0000	2.475	2.475	0.000
1090	0.0550	0.0545	0.0005	2.750	2.725	0.025
1091	0.0585	0.0590	0.0005	2.925	2.950	0.025
1092	0.0340	0.0340	0.0000	1.700	1.700	0.000
1095	0.0085	0.0080	0.0005	0.425	0.400	0.025
1097	0.0112	0.0113	0.0001	0.560	0.565	0.005
1098	0.0143	0.0145	0.0002	0.715	0.725	0.010
1100	0.0445	0.0450	0.0005	2.225	2.250	0.025
1101	0.0475	0.0480	0.0005	2.375	2.400	0.025
1102	0.0483	0.0478	0.0005	2.415	2.390	0.025
1103	0.0055	0.0052	0.0003	0.275	0.260	0.015
1104	0.0400	0.0403	0.0003	2.000	2.015	0.015
1105	0.0080	0.0080	0.0000	0.400	0.400	0.000

The carcasses of some newly born pigs were ashed after air drying and dissolved in nitric acid, the phosphoric acid precipitated as ammonium phosphomolybdate and the filtrate analyzed for calcium in the same way. Following are the results obtained:

TABLE III.—ANALYSIS OF PIG CARCASSES<sup>2</sup> FOR CALCIUM.

Lab. No. of sample.	Gram CaO found in aliquots.			% Ca in original sample <sup>3</sup> (according to aliquots).		
	No. 1.	No. 2.	Diff.	No. 1.	No. 2.	Diff.
1255	0.0377	0.0377	0.0000	7.54	7.54	0.00
1256	0.0372	0.0372	0.0000	7.44	7.44	0.00
301	0.0370	0.0360	0.0010	7.40	7.20	0.20
303	0.0413	0.0407	0.0006	8.26	8.14	0.12
308	0.0408	0.0408	0.0000	8.16	8.16	0.00
309	0.0348	0.0352	0.0004	6.96	7.04	0.08
310	0.0345	0.0345	0.0000	6.90	6.90	0.00
315	0.0352	0.0348	0.0004	7.04	6.96	0.08
316	0.0403	0.0405	0.0002	8.06	8.10	0.04
317	0.0388	0.0382	0.0006	7.76	7.64	0.12
321	0.0418	0.0420	0.0002	8.36	8.40	0.04

<sup>1</sup> 2-gram samples taken.

<sup>2</sup> Ashing of the pig samples was done in platinum dishes. No calcium acetate or magnesium nitrate was added during ashing as it was found to be unnecessary.

<sup>3</sup> The weight of the air-dried sample taken in each case was 0.5 g.

When iron and aluminium were removed according to the description of Shedd<sup>1</sup> and tested for molybdenum in a series of four determinations the test was positive. Because of the fact that iron is titrated with permanganate after fusion with potassium bisulfate and reduction with nascent hydrogen, some complications may arise, preventing accurate results.

More reliable and accurate results of all basic ions in ash of forage plants and animal carcasses are obtained if the excess of molybdenum after the removal of  $P_2O_5$  as ammonium phosphomolybdate, is removed as sulfide according to Fresenius.<sup>2</sup> In short, the filtrate is made slightly ammoniacal, digested with colorless ammonium sulfide, carefully acidified with 12% hydrochloric acid, warmed to  $45^\circ$  to flocculate the molybdenum sulfide and filtered through a Schleicher & Schüll filter (blue label). The clear filtrate thus obtained is boiled to expel hydrogen sulfide and after further filtration is ready for basic analysis. The fact that a perfect separation and gravimetric estimation of iron and aluminium can be effected with the use of this method, makes it highly commendable. Moreover, if manganese is present in traces, it may easily be tested for and estimated. Some work was undertaken in this laboratory to show the advisability of substituting this method for the separation and estimation of basic ions in ash in place of the official methods, giving special consideration to the time required and also accuracy. Aliquots of a solution of calcium nitrate of known strength were mixed with a solution of disodic hydrogen phosphate and the phosphorus removed as phosphomolybdate. From the filtrate thus obtained, molybdenum was removed as sulfide according to directions given above. The calcium was precipitated as oxalate and ignited into oxide. Following are the results obtained under these conditions:

TABLE IV.—ESTIMATION OF CALCIUM AFTER REMOVAL OF MOLYBDENUM AS SULFIDE.

No. of the experiment.	Gram CaO taken as $Ca(NO_3)_2$ .	Gram CaO found.	Error, g.	No. of the experiment.	Gram CaO taken as $Ca(NO_3)_2$ .	Gram CaO found.	Error, g.
1	0.0536	0.0535	-0.0001	11	0.0524	0.0525	+0.0001
2	0.0536	0.0537	+0.0001	12	0.0524	0.0520	-0.0004
3	0.0536	0.0534	-0.0002	13	0.0524	0.0522	-0.0002
4	0.0536	0.0539	+0.0003	14	0.0524	0.0523	-0.0001
5	0.0536	0.0540	+0.0004	15	0.0524	0.0522	-0.0002
6	0.0536	0.0534	-0.0002	16	0.0524	0.0522	-0.0002
7	0.0536	0.0540	+0.0004	17	0.0524	0.0520	-0.0004
8	0.0536	0.0530	-0.0006	18	0.0524	0.0515	-0.0009
9	0.0536	0.0532	-0.0004	19	0.0524	0.0521	-0.0003
10	0.0536	0.0532	-0.0004				

The time required in this case is much shorter than when basic acetate method is used, three hours being sufficient to bring one series of six, each

<sup>1</sup> O. M. Shedd, *Bur. of Chem., Bull.* 152, pp. 63, 64.

<sup>2</sup> Fresenius' *Quant. Chem. Anal.*, 1, 464.

having one duplicate, to the condition where calcium is ready for precipitation as oxalate.

### Summary.

A more rapid and accurate method is recommended for the determination of calcium in the ash of agricultural products. It consists essentially in removing the phosphorus as ammonium phosphomolybdate from an acid solution of the ash, and precipitation of calcium from the filtrate as calcium oxalate, either directly or after the removal of the excess of molybdenum as sulfide. Since no advantage was found in removing the molybdenum, it is recommended that this step be omitted.

A comparison of this method with the so-called basic acetate method in common use brings out the following points in its favor:

1. It yields more accurate and concordant results than the basic acetate method.
2. No attention need be given to the maintenance of exact neutrality of the solution.
3. The volume of the filtrate resulting from the precipitation of phosphorus can be kept reasonably small, so that no evaporation is necessary.
4. The time required for the determination is greatly shortened.
5. Phosphorus and calcium may be determined in the same aliquot.

AMES, IOWA.

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## [CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF ILLINOIS.] A SYSTEMATIC SEPARATION OF THE ANIONS OF GROUP I. ANIONS WHOSE SILVER SALTS ARE INSOL- UBLE IN NITRIC ACID.<sup>1</sup>

By H. C. P. WEBER AND H. A. WINKELMANN.

Received August 17, 1916.

The customary methods for the examination and separation of the acids depend mainly upon various group reactions, followed by specific tests for one or the other anion, combined with a process of elimination based upon the results of the analysis for the cations. For a limited number of anions special methods of separation have been worked out in detail, as for instance for certain of the acids containing sulfur. The literature on the separation of the halogens Cl, Br, I, is quite voluminous and in this particular case a choice of various satisfactory methods of separation is possible. On the whole these methods are, however, limited in scope and very little work has been done upon systematic methods for the separation of the anions.<sup>2</sup>

<sup>1</sup> Portions of this work were submitted by Mr. H. A. Winkelmann in partial fulfillment of the requirements for the degree of Master of Science in Chemistry in the Graduate School of the University of Illinois, June, 1915.

<sup>2</sup> The lack of such a systematic procedure is shown particularly by the errors and confusion resulting from the customary method of attack in the hands of students



The classification of acids into groups according to their reactions with silver and barium salts, frequently used in texts on qualitative analysis is ascribed to Bunsen in 1878, and is used practically unchanged. In 1900 Abegg and Herz<sup>1</sup> described, very briefly, a separation of the anions based upon the solubility of the calcium, barium and zinc salts and the volatility of various acids.

Quite recently A. A. Noyes,<sup>2</sup> published the most comprehensive scheme of separation of the anions so far elaborated. The fundamental idea of this method is the separation of the volatile and nonvolatile acids in various stages by distillation after addition of phosphoric acid. The more volatile acids, such as hydrocyanic acid, are collected in the first distillate, the less volatile in the second. The various portions are then examined for specific reactions of one or the other acid, without attempting to effect a further separation. The method is, in many respects, ideal and very effective, and a very great improvement upon the method of trial and failure indicated above.

In cases in which the nature of the mixture is such that interaction between the various constituents is possible, the prolonged heating during distillation will hasten and extend decomposition, with resulting decrease of directness or certainty in the results.<sup>3</sup>

The part of the investigation here described has to do with the first group of acids, in the following classification:

I. Anions which give silver salts insoluble in dilute nitric acid, but whose barium salts are soluble in water or acids.

II. Anions which give silver salts difficultly soluble in neutral solution, but readily soluble in dilute nitric acid, and whose barium salts are readily soluble.

III. Anions which give silver and barium salts insoluble in water alone, but soluble in the presence of dilute nitric acid.

IV. Anions which give salts of silver and barium readily soluble under all conditions.

V. Anions which give silver salts soluble in water, but whose barium salts are insoluble, even in the presence of nitric acid.

first confronted with the problem of recognizing, and distinguishing between the various negative radicals in an unknown mixture. While they obtain a fairly comprehensive view of the relations between the various metallic elements in their reactions, this is not true of the nonmetallic elements.

<sup>1</sup> *Z. anorg. Chem.*, 23, 236 (1900).

<sup>2</sup> *THIS JOURNAL*, 34, 609 (1912).

<sup>3</sup> The fact that each distillation with phosphoric acid entails destruction of the distillation flask does not involve more than a slight inconvenience in individual cases; where the method is, however, to be applied repeatedly by large numbers of students, this factor does become one which it is desirable to eliminate.

The anions included in this first group are  $\text{Cl}^-$ ;  $\text{Br}^-$ ;  $\text{I}^-$ ;  $\text{CN}^-$ ;  $\text{CNS}^-$ ;  $\text{Fe}(\text{CN})_6^{\text{III}}$ ;  $\text{Fe}(\text{CN})_6^{\text{IV}}$ ;  $\text{S}^-$ .

The first step in the problem consisted in the examination of the solubility data of the salts of the various anions, either in neutral, acid or alkaline solutions and in the presence of various salts. While it was a simple matter to find numbers of insoluble salts, the compounds available rapidly narrow down in number, either because they are not suitable for purposes of separation, or because the solubilities referred to pure salts in equilibrium with pure water, conditions which are not applicable always to the conditions of an analysis. For this reason a number of the cases examined as promising, but found to be unsatisfactory, are briefly described as a matter of record. The effect of the complications introduced in the course of analysis is shown by the results tabulated under these and various other metals further on.

**Ferrocyanides and Ferricyanides.**—The plan which first suggested itself was to add metallic zinc to the mixture of the silver salts of the acids. The silver salts would thus be reduced with the production of metallic silver and the corresponding zinc salts. The zinc ferrocyanide and ferricyanide being insoluble, would remain with the reduced silver and unused zinc, the remaining zinc salts being left in solution. This method lost in sensitiveness as a result of the occlusion of some of the other anions by the metallic silver or zinc. In addition,<sup>1</sup> metallic zinc, when acting on potassium ferricyanide, will reduce the same, yielding some ferrocyanide, and in part replacing iron in the complex.

This procedure would have been more in harmony with the steps to be anticipated in the succeeding groups, since the first group could thereby be removed as a whole, but was not found feasible. The difficulty was overcome by adding zinc nitrate to the solution before adding silver nitrate. The insoluble zinc ferrocyanide and ferricyanide are precipitated, leaving the remaining acids of the first group in solution, from which they are precipitated by silver nitrate. Experiments performed to determine the sensitiveness of this method showed that in a solution containing dilute nitric acid, 0.05 mg. of ferricyanide, or ferrocyanide, in 10 cc. total volume, gave a decided precipitate, while 0.02 mg. could still be detected by an experienced observer. The separation of the two zinc salts was found to be readily effected by means of ammonium hydroxide, and will be described under the general procedure.

**The Remaining Anions.**—Having precipitated the silver compounds of  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{CN}^-$ ,  $\text{CNS}^-$ , and  $\text{S}^-$ , the next step was to determine upon a process of separation and identification. The following steps were investigated for their usefulness:

*A. Ammonium Hydroxide.*—Since ammonium hydroxide is a good sol-

<sup>1</sup> vide G. McP. Smith, *Z. anorg. Chem.*, **82**, 65 (1913).

vent for some silver salts, the possibility of its use for the separation was examined. Silver iodide and sulfide were found to be insoluble under all conditions. The solubility of the silver salts under examination depends considerably upon conditions, as is well known, making necessary a careful control of the variables. For example, silver chloride is easily soluble in dilute ammonium hydroxide, whereas the bromide is but slightly so, but its solubility increases materially with the concentration of the ammonia. The thiocyanate is soluble only in concentrated ammonia. The ammonium cyanide, on the other hand, is very unstable, so that even if a separation is obtained, there is danger of decomposition in subsequent manipulations.

One of the fundamental objections to this method is the unreliability of results which depend upon extraction of a more soluble substance from an admixture containing less soluble substances. This is never possible with mathematical precision, and, unless the differences in solubility are very great, it is not even possible for practical purposes. Given large quantities of two constituents, for instance silver bromide and silver iodide, such a method gives decided results. But at the extremes of the range of mixtures, the results are of necessity erroneous. Thus a large quantity of iodide will prevent solution of small percentages of bromides, and conversely, small percentages of iodide will dissolve with the larger portion of bromide. Methods of separating the silver halides by means of ammonium hydroxide do not seem to have obtained wide application, although several have been described. For these reasons, the method was abandoned after a brief examination of its possibilities.

*B. Lead Salts.*—The behavior of the lead salts of this group of acids was examined with the view to separating iodine as lead iodide, after the reduction of the silver salts. The following table shows the behavior of lead acetate added to a neutral and acid solutions of the anions:

TABLE I.—BEHAVIOR OF LEAD ACETATE WITH VARIOUS SALTS<sup>1</sup> (VOL. 10 Cc.).

	Solution neutral.					Solution acid (1-2 cc. dil. HNO <sub>3</sub> ).				
	1 mg.	3 mg.	5 mg.	7 mg.	10 mg.	1 mg.	3 mg.	5 mg.	7 mg.	10 mg.
KCl.....	+	+	+	+	+	—	—	—	—	—
KBr.....	+	+	+	+	+	—	—	—	—	—
KI.....	+	+	+	+	+	—	—	—	+	+
KCN.....	+	+	+	+	+	—	—	—	—	—
KCNS.....	+	+	+	+	+	—	—	—	—	—

The results given in Table I show that this salt does not offer a satisfactory means of separation, since in neutral solutions a precipitate was obtained in every case, while in an acid solution, 7 mg. of iodide yielded only a slight precipitate and 10 mg. only a fair one. Even if the lead iodide separation had been practicable, the lead would again have to be removed

<sup>1</sup> In this and subsequent tables a plus sign indicates a positive test and a minus sign a negative result.

after proceeding with another step. Such an extra step increases the liability of losing small amounts of the acid, which was considered an added disadvantage in the use of lead.

*C. Mercurous Salts.*—The insoluble halide compounds of univalent mercury were next examined for their usefulness. One milligram of chloride or bromide ion in 10 cc. of a solution acidified with nitric acid gave, as anticipated, a decided precipitate with mercurous nitrate. Corresponding or larger quantities of the iodides, cyanides or thiocyanates gave precipitates from neutral solutions which readily redissolved upon acidification or addition of excess  $\text{HgNO}_3$ . In fact, even the mercurous chloride dissolves in a large excess of mercurous nitrate in an acidified solution. In the hope of separating the constituents of the silver precipitate by treatment with mercurous nitrate,  $\text{AgCl}$ ,  $\text{AgBr}$ ,  $\text{AgI}$ ,  $\text{AgCN}$  and  $\text{AgCNS}$  were digested with  $\text{HgNO}_3$ . The precipitates were found to be reduced, the presence of mercurous chloride and bromide in the precipitate being indicated by the blackening of the residue by ammonia. The remaining three anions were found in the mercurous solution. Part of the chloride and of the bromide were, however, also in solution, the recovery of the cyanide ion was not satisfactory and the method involved subsequent removal of mercury for further steps. This procedure was therefore abandoned in favor of the formate reduction.

*D. Formate Reduction.*—In order to effect a separation of the precipitated silver salts, various reducing agents were investigated. Copper and metallic zinc reduce all of the silver compounds with the exception of the sulfide. Formaldehyde in alkaline solution acts in the same manner. Formates in acid solution give slow and incomplete reduction. It was soon found that with proper control of the alkalinity a satisfactory separation of chlorine could be obtained. The iodide of silver is the most resistant and even with the greatest concentration of alkali, silver iodide is practically unaffected. With solutions containing 15% of sodium hydroxide the reduction of silver chloride to metallic silver is very rapid, 200 mg. of silver chloride being completely reduced by warming a few minutes, whereas the bromide is only very slightly affected. In a solution which contains about 8% of sodium hydroxide and sodium formate, silver chloride was completely reduced in 10 minutes' boiling, while the bromide is unaffected even after much longer treatment. The cyanides and thiocyanates were reduced under the same conditions. Cyanides caused some difficulty by dissolving in the known fashion in the alkali, so that the filtrate from the silver residue contained some silver cyanide in addition to sodium cyanide. This caused some difficulty in the succeeding manipulations, which was later overcome by removing the silver cyanide from the silver chloride, bromide, iodide, and thiocyanate before reduction. This can be very effectively done by treatment with a

solution of a mercuric salt, without dissolving any of the other silver compounds, which behavior furnishes, at the same time, a very satisfactory method of isolating and detecting the cyanide radical. The reaction depends upon the fact that mercuric cyanide is dissociated to an abnormally low extent into cyanide ion, as the well-known anomalous behavior of mercury cyanide indicates. If silver cyanide is digested with mercuric nitrate or sulfate it immediately dissolves, or conversely, in the presence of mercuric salts cyanides do not precipitate silver salts. This behavior is most pronounced with cyanides, the remaining anions of this group precipitating the corresponding salts of silver even in the presence of mercury, provided certain precautions are observed.

In connection with these experiments the ferri- and ferrocyanide of silver were also subjected to reduction by means of formates in the presence of alkalis, with the view to include these two ions in the silver precipitate for further treatment. This would then have avoided the precipitation of these two anions by means of the zinc before adding silver nitrate. The procedure was not however applicable. The two silver salts were reduced, but the alkaline filtrate gave either uncertain, or negative, tests for ferrocyanide or ferricyanide. Here, as with such reducing agents as copper and zinc, the complex cyanide radical suffers disruption yielding, among other things, the cyanide ion. This behavior made it necessary to remove the complex cyanides at the beginning of the separation.

Applying, then, sodium formate as a reducing agent to the mixture of silver salts, after dissolving silver cyanide by means of a mercuric salt, causes reduction of silver chloride and silver thiocyanate, with the formation of metallic silver in the residue, and the corresponding sodium salts in solution. From this solution the thiocyanate can readily be precipitated as cuprous thiocyanate under the proper conditions, and the filtrate from this precipitate tested for chloride by means of silver nitrate.

The residue from the reduction contains metallic silver and any silver bromide, iodide and sulfide originally present.

**Cuprous Salts.**—The original procedure which was developed entailed the separation of chloride, bromide, cyanide and thiocyanate after the silver salts had been converted into the corresponding sodium salts by means of reduction with formate. The precipitation of copper thiocyanate is a well-known quantitative method. It remained to be seen how the chloride and bromide behaved under the conditions of separation. It was found that, in the presence of sulfurous acid, 100 mg. of chloriae or bromine (as potassium salts) are held in solution. Under the same conditions 0.02 mg. of CN or CNS give a decided precipitate.<sup>1</sup>

<sup>1</sup> While working on this method a paper by Curtman and Wickoff, *THIS JOURNAL*, 37, 298 (1915), appeared, treating the determination of bromides in the presence of cyanides, thiocyanates and ferricyanides. The results there were in harmony with

While this gave a satisfactory separation from bromine the question of separation of the cyanide and thiocyanate still remained, and caused considerable difficulty. The cobalt and nickel salts offered some hope for a separation but were rejected after trial. The cyanide may be converted into Prussian blue in one part of the solution and the characteristic ferric thiocyanate reaction obtained in another, but this was not all that could be desired, particularly when both constituents were present in rather large quantities. Fortunately, later work showed that the removal of the cyanide at an earlier stage of the procedure eliminated this difficult separation and this was therefore accepted as a welcome simplification of the process.

As a consequence of these results the best procedure was decided to consist in limiting this separation by means of cuprous salts to the removal of thiocyanates from chlorides. This process can be conveniently and accurately carried out and the other anions are provided for at other stages of the procedure.

#### PROCEDURE.

##### Precipitation of Ferricyanides and Ferrocyanides.

**Procedure I.**—Add one to three cc. of dilute nitric acid to a nearly neutral mixture of acids, and *immediately* enough zinc nitrate to insure complete precipitation of the ferricyanide and ferrocyanide and shake the solution vigorously. Completeness of the precipitation is indicated by a noticeable change in the character of the precipitate, which is colloidal at first but coagulates more readily when excess of precipitant is present. When sufficient ferricyanide is present to color the solution, there is a fairly sharp end point, consisting in the discharge of the yellow color. When not enough zinc nitrate is present the solutions are colloidal; an excess of zinc nitrate to insure complete precipitation of the ferricyanide and ferrocyanide is advantageous. One to two grams of ammonium nitrate hasten coagulation of the colloidal precipitate and should be added if difficulty is experienced in filtering.

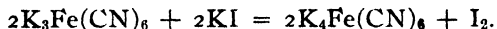
Heating the solution should be avoided, since it increases the tendency of the precipitate to become colloidal, and would cause loss of hydrocyanic acid. Ageing always favors the separation of colloidal precipitates, and should the precipitate run through the filter, which for this case should be a fairly close-grained one, it may be set aside for a short period and will then usually be found to have changed sufficiently to permit satisfactory filtration. The *same effect* may be obtained more rapidly by shaking the suspended precipitate energetically in a stoppered flask. Shaking, in effect, simply hastens the ageing of the colloid and is very  
our experience and showed that 2 mg. of bromine could be detected in the presence of as much as 500 mg. of the other constituents by applying the cuprous salt separation previous to the test.

effective in producing a precipitate which does not run through the filter.

When iodides and ferricyanides are both present, iodine will be liberated slowly. This does not interfere with the subsequent detection of iodine. In order, however, to check appreciable reduction of the ferricyanide to ferrocyanide the zinc nitrate should be added immediately, or, preferably, the nitric acid should be added first to the zinc nitrate and the two reagents added to the solution in one operation.

After washing the zinc precipitate on the filter several times with a few cubic centimeters of a dilute ammonium nitrate solution (rejecting all but the first washing), pour 10 cc. of a warm 3% NaOH solution through the filter. This is sufficient for quantities up to 200 mg. of each of the two salts, which dissolve, yielding the alkali ferri- and ferrocyanide and sodium zincate. Add to the resulting solution 5 cc. of a 5% ammonium nitrate solution, a few drops of zinc nitrate solution to provide excess zinc ion, and shake vigorously. The zinc ferrocyanide is precipitated as a gelatinous white precipitate. This precipitate is quite characteristic. It may, if desired, be further characterized by the conversion into the cupric or ferric ferrocyanide. The red cupric ferrocyanide is to be preferred, since it is just as sensitive and cannot be confused with the ferrous ferricyanide as the ferric ferrocyanide may. In either case, the ferrocyanide of zinc is dissolved in a small quantity of NaOH solution, the copper or iron is added and the solution then acidified. This is preferable to acidifying first, particularly when only small quantities are present, since the zinc ferrocyanide, when once formed, is not converted into the copper or iron salt very rapidly.

The ferricyanide is identified by acidifying the filtrate from the zinc ferrocyanide with dilute hydrochloric acid, and adding 1-2 cc. of potassium iodide solution (which should not give free iodine upon acidification), and 0.5-1 cc. of  $\text{CHCl}_3$  or  $\text{CCl}_4$ . The ferricyanide is reduced, giving free iodine in the  $\text{CHCl}_3$  layer.



The voluminous nature of these zinc precipitates adapts them particularly well to quantitative approximations. A series of seven precipitates obtained in the regular course of analysis and varying from 100 to 1 mg. in approximately even steps, were correctly estimated by four out of five observers entirely unused to the method. The same thing is true of the ferricyanide of zinc.

The iodide reaction develops rather slowly with small quantities (0.5 mg.) of ferricyanide but it is recommended in preference to the test with ferrous iron.

A ferric salt gives with a ferrocyanide a blue precipitate of ferric ferrocyanide, but not with ferricyanide. A ferrous salt gives with a ferricyanide a similar blue precipitate of ferric ferrocyanide. It gives with ferrocyanide a white precipitate of ferrous ferrocyanide when no ferric salt is present, but a blue one after exposure to the air. In order to distinguish the ferricyanide from ferrocyanide with a ferrous salt the solution must be fresh, that is, free from ferric salt. The reaction with potassium iodide is to be preferred for the reason that there is no possibility of confusion with ferro-

cyanide due to faulty separation. When applying this test for small quantities, it is necessary to bear in mind that commercial iodides usually contain traces of iodates and will consequently give traces of free iodine on acidification. A reagent which will not liberate iodine upon acidification may very conveniently be made by boiling a neutral, or but faintly acid, solution of potassium iodide with metallic magnesium.

The oxidation of iodides by ferricyanides is slow, and in testing for small quantities, time must be given for the iodine to be liberated. As in the case of ferrocyanide, a fairly accurate quantitative estimation can be made even by one unused to the method when amounts from 100 to 1 mg. are used.

The results obtained during experimentation on the above separation are given in Table II.

TABLE II.—SENSITIVENESS OF TEST WITH ZINC NITRATE IN PRESENCE OF DILUTE  $\text{HNO}_3$  (VOL. 10 Cc.).

Milligrams.	10	8	6	4	2	0.5	0.1	0.02
$\text{K}_3\text{Fe}(\text{CH})_6$ ....	+	+	+	+	+	+	+	+
$\text{K}_3\text{Fe}(\text{CN})_6$ ....	+	+	+	+	+	+	+	+

RELIABILITY OF SEPARATION FOR 0.1 MG. IN THE PRESENCE OF 200 MG. OF ANY ONE OF THE REMAINING ANIONS OF THIS GROUP (VOL. 10 Cc.):

$\text{K}_3\text{Fe}(\text{CN})_6$ ....	+	+	+	+	+	+	+	+
$\text{K}_3\text{Fe}(\text{CN})_6$ ....	+	+	+	+	+	+	+	+

### Precipitation of Silver Salts.

**Procedure II.**—The filtrate from the zinc precipitation is treated with silver nitrate until no further precipitate forms. If cyanides are present in appreciable quantities the disappearance of the odor of hydrocyanic acid indicates completeness of precipitation. A slight excess of silver nitrate is added, the precipitate is coagulated by shaking, and the solution is removed by decantation or filtration. The precipitate is washed with distilled water containing a few drops of nitric acid until the washings are practically free from silver. Reject all but the first washings. The solution contains the acids of subsequent groups. The precipitate is examined for  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{CN}^-$ ,  $\text{CNS}^-$ , and  $\text{S}^-$ .

### Separation of Cyanide.

**Procedure III.**—To the precipitated silver salts contained in a beaker, after having removed excess of water, add 2 cc. of a 2 molar solution of mercuric acetate containing 5% of acetic acid. Digest 15 minutes on the steam bath (the solution may be permitted to evaporate to dryness). Add 2 cc. of a 2 molar sodium acetate solution and dilute to 20 cc. and filter. The filtrate contains the cyanide as a complex mercury compound.  $\text{H}_2\text{S}$  is passed into this until mercury has been completely precipitated and the mercuric sulfide is removed by filtration. The filtrate is made alkaline with a few drops of sodium hydroxide, enough ammonium polysulfide is added to color the solution yellow (2–5 drops are sufficient unless very large quantities of cyanides are present) and it is then digested on the steam bath, preferably until the liquid has evaporated.



Enough dilute sulfuric acid is added to decompose the excess polysulfide. In the filtrate from this, which now contains thiocyanic acid, the blood-red color of ferric thiocyanate is obtained upon addition of ferric salts. (See Table VI.)

All of the halogen salts of silver dissolve in mercuric salts with the formation of highly complex mercuric compounds. Thus, in a solution containing one mol of  $\text{Hg}(\text{NO}_3)_2$  and one mol of  $\text{HNO}_3$ , 7 g. per liter (0.05 mol) of silver chloride, 7 g. (0.04 mol) of silver bromide and 25 g. (0.11 mol) of silver iodide will dissolve.<sup>1</sup>

The compounds formed are, according to the conditions, any one or all of the following:  $\text{HgHgCl}_4$ ,  $\text{HgHgCl}_2(\text{NO}_3)_2$ ,  $\text{AgHgCl}_2(\text{NO}_3)_2$ . As may be noted on comparing the remaining halides, the complex formation increases toward the iodide, *i. e.*, as the acid grows weaker. With the very weak hydrocyanic acid the complex formation is very much greater still, the  $\text{CN}^-$  being used up quantitatively to form either the  $\text{Hg}(\text{CN})_4^{2-}$  or the  $\text{Hg}(\text{CN})_3^-$  ion.<sup>2</sup> If, instead of using mercuric salts of the strong acids, the acetate is used the complex cyanide alone is formed, *i. e.*, only silver cyanide and not the chloride dissolves. (A trace of chloride, and more iodide, dissolves if a slight amount of acetic acid is present, either added or from hydrolysis, but this is completely stopped by the addition of sodium acetate to the solution, so that not even 0.2 mg. of iodine dissolves in 300 times as much mercuric acetate.) In effect, then, mercuric acetate is less complex than mercuric cyanide and more so than the remaining halogen compounds and this makes the separation possible. The addition of the sodium acetate after digestion with the acid solution of mercuric acetate is necessary to precipitate the last traces of the other halides.

For the final characterization of the cyanide, the thiocyanate conversion works well, 0.1 mg. being detected without difficulty. Removal of mercury from the solution by means of more electropositive metals and conversion of the cyanide into ferrocyanide gave erratic results under the conditions prevailing and is not to be recommended here.

### Separation of Chloride and Thiocyanate.

**Procedure IV.**—To the washed silver salts, from which the cyanide has been removed (excess water should be decanted), add 10–15 cc. of an 8% sodium hydroxide solution and 1 g. of sodium formate and boil a short time in a covered receptacle (5 to 10 minutes). Dilute to 20 cc., decant or filter and test the filtrate for chlorine and thiocyanate as follows: very nearly neutralize the solution with dilute sulfuric acid, completing the neutralization with sulfurous acid. To the acid solution, which should smell decidedly of  $\text{SO}_2$ , add copper sulfate solution drop by drop until no more copper thiocyanate is precipitated. Filter, dissolve the precipitate in hydrochloric acid and add a ferric salt to obtain the red ferric thiocyanate. To the filtrate from the cuprous thiocyanate add dilute nitric acid equivalent in quantity to the sulfurous acid previously added, heat until the  $\text{SO}_2$  is driven off and add silver nitrate until no more silver chloride forms. (See Table VI.)

The precipitation of thiocyanates by copper in a reducing solution is very nearly complete, only  $5 \times 10^{-4}$  g. dissolving in a liter. If desired, a separate portion of the solu-

<sup>1</sup> Morse, *Z. physik. Chem.*, **41**, 707 (1902).

<sup>2</sup> Sherfill, *Ibid.*, **43**, 705 (1903); **47**, 103 (1904).

tion may be tested for thiocyanate directly with a ferric salt. If found present it must first be removed before testing for chloride.

Formic acid reduces silver chloride to metallic silver much more readily than it does the bromide or the iodide. The speed of reduction varies considerably with the concentration of the sodium hydroxide. For this reason the solution should not be allowed to concentrate to an appreciable extent while heating. For the reduction it is advisable to prepare a reducing solution containing 8 g. NaOH and 10 g. of  $\text{H.COONa}$  (chlorine free) per 100 cc. and to use 20 cc. of this solution. With the concentrations given, silver chloride is completely reduced in 10 minutes' vigorous boiling, while silver bromide is not affected. With a 15% sodium hydroxide solution and as much as a half hour's boiling silver bromide is partially reduced (a few per cent of 200 mg. for instance) while silver iodide is not appreciably reduced even in 33% NaOH on long extended boiling. The silver thiocyanate behaves toward the reduction as the chloride does, forming sodium thiocyanate, which dissolves, and metallic silver.

### Separation of Bromide and Iodide.

**Procedure V.**—The precipitate which remains contains silver bromide, iodide (and sulfide) and in addition the metallic silver resulting from the previous reduction. It is covered with a few cubic centimeters of concentrated ammonia and metallic copper in powder form (molecular copper) is added. The reduction of the bromide and iodide is instantaneous, the corresponding cuprous salts going into solution. If a precipitate of basic copper salts is formed more  $\text{NH}_4\text{OH}$  must be added. Silver sulfide remains behind. The filtrate is neutralized with sulfurous acid and an excess of dilute sulfuric acid is added. If iodine is present white copper iodide is precipitated. This is collected on the filter (shake precipitate to coagulate) and the iodine, after dissolving the cuprous iodide in hydrochloric acid, is liberated by chlorine water (or  $\text{HNO}_2$ ,  $\text{H}_2\text{O}_2$  or  $\text{FeCl}_3$ ) and dissolved in carbon tetrachloride giving a violet color.

To the filtrate from the copper iodide, which contains the bromide, nitric acid is added and the solution is warmed until most of the  $\text{SO}_2$  has been driven off. Addition of silver nitrate then causes formation of yellowish silver bromide. (See Table VI.)

The precipitation of copper as cuprous iodide is a well-known quantitative method, the solubility of  $\text{Cu}_2\text{I}_2$  in water being only  $3 \times 10^{-4}$  g. per liter. Under the same conditions 100 mg. of bromine are not precipitated. The characterization of the precipitate is hardly necessary unless it is feared that the thiocyanate was not completely removed in the previous step, or unless unusually large quantities of bromide were taken.

### Detection of Sulfide.

**Procedure VI.**—The silver residue from the reduction contains the sulfide. It is completely dissolved in nitric acid. The silver sulfide dissolves with formation of sulfuric acid, which, after dilution to 100 cc. is precipitated as white barium sulfate upon addition of barium nitrate.

# Numerical Data.

TABLE III.

## Formate Reduction.

4 Millimols of the silver salts (AgCl, AgBr, etc.) 2 g. H.COONa + NaOH  
(vol. 20 to 40 cc.).

% NaOH.	6.	8.	11.	14.	16.	18.
AgCl.....	Not complete	Reduced	Reduced	Reduced (10 min.)	Reduced	Red. cold
AgCN, AgCNS..	.....	Reduced	.....	.....	.....	.....
AgBr.....	Not red.	Not red.	Not red.	Not red.	Trace red.	Slight red. in 2 1/2 hr.
AgI.....	.....	.....	.....	.....	No trace of reduction.	

TABLE IV.

Rate and completeness of reduction with copper powder.

200 mg. (8 millimols) Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, CN<sup>-</sup>, CNS<sup>-</sup> as the silver salts, freshly precipitated and washed. Various ions were taken separately.

Set. 1. Copper, about equal in volume to the silver precipitate and distilled water. The silver salts are reduced rapidly to metallic silver.

Set. 2. Same as 1, and 1 cc. of conc. ammonia added. The reduction is very rapid (less than 10 minutes). The residues of silver and copper after washing dissolved without a trace of residue in dilute nitric acid. If air is excluded during the operation the ammonia solution contains the cuprous compounds.

Set. 3. Same as 1 but carried out in presence of dilute sulfuric acid. Reduction takes place much more slowly and is not complete, even on long standing.

Set 4. Similar trials with Pb as reducing agent gave unsatisfactory results.

TABLE V.

## Mercuric salt separation of cyanides.

Solubility of silver salts.—To 5 cc. of 0.5 M HgNO<sub>3</sub> about 1 cc. of 1.5 M AgNO<sub>3</sub> was added. In order to obtain a precipitate, 2.5 mg. Cl<sup>-</sup>, 0.8 mg. Br<sup>-</sup>, 4 mg. I<sup>-</sup>, no pptd. CN<sup>-</sup>, 1 mg. CNS<sup>-</sup> were added before a precipitate formed. Addition of sodium acetate caused immediate precipitation of the dissolved silver salt, except in the case of AgCN.

Similar behavior was noted with HgSO<sub>4</sub> + H<sub>2</sub>SO<sub>4</sub> solution.

To 20 cc. of 0.2 M mercuric acetate a few drops of acetic acid and silver nitrate was added. In order to obtain a precipitate the following amounts of halogen were necessary: 0.4 mg. Cl<sup>-</sup>; 0.5 mg. Br<sup>-</sup>; 0.6 mg. I<sup>-</sup>; no ppt. w. CN<sup>-</sup>; 0.2 mg. CNS<sup>-</sup>. To the same solution 2 cc. 2 M sodium acetate were added. Precipitates were obtained with 0.04 mg. Cl<sup>-</sup>; 0.04 mg. Br; 0.02 mg. I<sup>-</sup>; no ppt. w. CN<sup>-</sup>; 0.01 mg. CNS<sup>-</sup>. The precipitates obtained under the last conditions were practically as strong as the blanks obtained without HgC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> in distilled water.

TABLE VI.

Sensibility of procedure as outlined with the various ions.<sup>1</sup> A long series of tests was made with varying quantities. Only the minimum amounts used are tabulated. Figures represent milligrams.

	Cl <sup>-</sup> .	Br <sup>-</sup> .	I <sup>-</sup> .	CN <sup>-</sup> .	CNS <sup>-</sup> .	Focy <sup>≡</sup> .	Ficy <sup>≡</sup> .
Other ions absent.....	0.04	0.04	0.02	0.05	0.05	0.02	0.02
200 mg. of any other ion present.....	0.10	0.10	0.10	0.10	0.10	0.10	0.10

TABLE VII.

Constitution of unknown solutions analyzed.

Mg.	A.	B.	C.	D.	E.	F.	G.	H.
Cl <sup>-</sup> .....	100	0	1	10	20	40	60	80
Br <sup>-</sup> .....	80	100	0	1	10	20	40	60
I <sup>-</sup> .....	60	80	100	0	1	10	20	40
CN <sup>-</sup> .....	40	60	80	100	0	1	10	20
CNS <sup>-</sup> .....	20	40	60	80	100	0	1	10
Ficy <sup>≡</sup> .....	10	20	40	60	80	100	0	1
Focy <sup>≡</sup> .....	1	10	20	40	60	80	100	0
Total .....	310							

Sets of solutions constituted as shown in Table VII were prepared and analyzed by H., J., and W., the contents being unknown to the analyst at the time. Since the results were uniformly correct they are not reproduced in detail. In Solution B chlorine was found in small amounts in every instance. This error is only an apparent one however, since the other salts present, while of high grade commercial quality were not chlorine-free. Thus no sample of cyanide was found during the course of the work which did not contain chlorine. In solution C, which contained 80 mg. I, one analyst reported a trace of bromine. In Solution H, ferrocyanide was twice reported although not added. Reduction of the ferricyanide by the hydriodic acid present, or a content of ferrocyanide in the ferricyanide, accounts for this. Otherwise the results obtained were correct.

### Summary.

A procedure is described in which any mixture of the ions Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, CN<sup>-</sup>, CNS<sup>-</sup>, FeCy<sub>6</sub><sup>≡</sup>, FeCy<sub>6</sub><sup>≡</sup> may be systematically separated with quantitative approximation.

Data in support of the proposed methods are furnished. The separations given are adequate when the respective ions form 0.01 to 0.0001 of the total, varying somewhat with the ion in question.

The procedure may be represented schematically by Table VIII, in which the compounds listed are empirical designations and an underscored substance indicates a precipitate. The numbers indicate the corresponding procedure:

<sup>1</sup> For convenience in these tables, ferrocyanide is designated by Focy and ferricyanide by Ficy.



[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE MONTANA EXPERIMENT STATION, UNIVERSITY OF MONTANA.]

### LEAD ARSENATES.

#### A STUDY OF THE FACTORS CONTROLLING THE REACTIONS OF LEAD NITRATE AND LEAD ACETATE WITH DISODIUM ARSENATE.

By G. ENNIS SMITH.

Received June 30, 1916.

Since Moulton<sup>1</sup> in 1893 first demonstrated the economic value of lead arsenate, numerous publications have appeared discussing the different compounds of lead and arsenic acid. These have dealt chiefly with the methods of preparation, the composition, some of the physical properties, and their efficiency as insecticides. While it has been generally stated that the composition varies with the source, mode of preparation, concentration, temperature, and every other conceivable condition that may vary in the production, yet there has been no attempt to define how these factors cause the variation; in fact, there has been a general evasion of even stating the direction and the extent to which the composition is influenced by the different factors.

The object of this paper will be to attempt to define the conditions in the production of lead arsenate that regulate the composition, and when the conditions are varied to demonstrate the influence that the variation will exert on the reaction, and on the composition of the resulting products.

It is not considered necessary to give a historical review of literature on lead arsenates as that has been given in a recent volume<sup>2</sup> of *THIS JOURNAL*. In general the various investigators have contended that the reaction of lead nitrate and disodium arsenate can be represented in the main by the equation



though the composition of the resulting lead arsenate would indicate that there was slight deviation and that the reaction of lead acetate with disodium arsenate can be represented closely by the equation



While working on another problem with commercial lead arsenates, some experiences suggested that the reactions given by the various investigators were not correct and that there might be a movable equilibrium in the products of the reactions, and thus a study of this problem was undertaken. Before reliable results could be obtained, however, it was necessary to prepare pure samples, at least of the lead and sodium compounds which may be components of the systems to be examined.

<sup>1</sup> Mass. Board, *Agr. Report*, 41, 282 (1893).

<sup>2</sup> Tartar and Robinson, *THIS JOURNAL*, 36, 1843 (1914).

### Experimental.

**Preparation of the Lead Compounds.**—Tartar and Robinson<sup>1</sup> claimed that they had prepared pure diplumbic arsenate, and a basic lead arsenate of a constant composition by the reaction of diplumbic arsenate with ammonium hydroxide. They stated that triplumbic arsenate is not formed under the ordinary aqueous conditions employed in the manufacture of commercial lead arsenate and that the precipitates obtained from the reactions of lead acetate and lead nitrate with disodium arsenate are mixtures of diplumbic arsenate and the basic lead arsenate.

When the results of Tartar and Robinson were examined it was observed that there was a great discrepancy. They claim that the composition of the basic lead arsenate, produced by the reaction of diplumbic arsenate with ammonium hydroxide, may be represented closely by the formula  $21\text{Pb}_3(\text{AsO}_4)_2 \cdot 2\text{Pb}(\text{OH})_2 \cdot 10\text{H}_2\text{O}$ . There are 65 Pb atoms and 42 As atoms in this formula and as the number of Pb and As atoms is identical in diplumbic arsenate, then it must be concluded that an amount corresponding to 23 atoms As or 35.38% of the arsenic of diplumbic arsenate has gone into solution. In outlining a method for a quantitative determination of diplumbic arsenate by the same reaction of diplumbic arsenate with ammonium hydroxide, they state that "the amount of soluble arsenic calculated as  $\text{As}_2\text{O}_5$  and then multiplied by the factor 7.6034, gives the amount of lead hydrogen arsenate," which would indicate that 39.71% of the arsenic of the diplumbic arsenate has gone into solution. On account of this discrepancy the reaction of diplumbic arsenate with ammonium hydroxide was studied.

The diplumbic arsenate was prepared from solutions of lead nitrate and disodium arsenate of equimolar proportions (concentration 0.01 *M*); when the precipitate had formed one-half the molecular proportion of nitric acid was added. After standing eighteen hours the supernatant liquid was decanted and the precipitate was then washed by decantation, first with water acidulated with nitric acid, then with distilled water, and dried at 110°. This is a modification of the method suggested by Tartar and Robinson. (The reason for the modification will be discussed later on.) By this method two samples were prepared which, on analysis, showed an arsenic content of 33.08% and 33.1% of  $\text{As}_2\text{O}_5$ , respectively, which would indicate that there had been a fairly complete isolation of diplumbic arsenate. When prepared in this manner diplumbic arsenate takes the form of comparatively large, transparent, crystalline plates, showing a general rhombohedral direction when seen through the microscope.

Weighed samples of the diplumbic arsenate were digested with a 5% solution of ammonium hydroxide on a steam bath for three hours. They

<sup>1</sup> *Loc. cit.*

were then filtered, washed, and dried at  $110^{\circ}$ . The amount of soluble arsenic in the filtrate, the loss in weight of the samples, and the lead and arsenic content of the dried insoluble residue were determined. It was noted that the soluble arsenic approached 40% of the arsenic of the diplumbic arsenate, therefore, in the products of the reaction the ratio of the soluble arsenic to the insoluble arsenic approaches two to three. Thus it may be that the reaction can be represented by the following equation:



TABLE I.

Analyses of the Products of the Reaction of Diplumbic Arsenate with Ammonium Hydroxide.

	Soluble arsenic in filtrate. Per cent.	Loss of wt. of the lead compound. Per cent.	Insoluble residue.	
			Lead as PbO. Per cent.	Arsenic as $\text{As}_2\text{O}_5$ . Per cent.
Sample No. 1.....	39.9	15.22	74.98	23.43
Sample No. 2.....	39.94	15.28	75.05	23.46
Theoretical for $\text{Pb}_5\text{OH}(\text{AsO}_4)_3$ .....	40.00	15.32	75.924	23.463
As found by Tartar and Robinson.....	39.71 <sup>1</sup>	.....	74.72 <sup>2</sup>	23.43 <sup>2</sup>
Theoretical for $21\text{Pb}_3(\text{AsO}_4)_2 \cdot 2\text{Pb}(\text{OH})_2 \cdot 10\text{H}_2\text{O}$ .....	35.38	.....	74.2	24.694
Theoretical composition of $\text{PbHAsO}_4$ .....	.....	.....	64.292	33.113

These results would indicate that the reaction can be represented by the above equation and that the formula  $\text{Pb}_5\text{OH}(\text{AsO}_4)_3$  more closely represents the insoluble product of the reaction of diplumbic arsenate with ammonium hydroxide, than the formula suggested by Tartar and Robinson.

The results of the lead determination do not correspond very closely with the theoretical, but it is generally accepted that the method of the Association of Official Agricultural Chemists for the determination of lead gives low results. For this reason, in this paper, more emphasis will be laid on the arsenic determination, and the results of the lead determination will be given only where it is considered to be essential. It might be inferred from the lead determination that it was a hydrated compound. Instead of carrying out a lengthy investigation of the lead determination, it was decided to determine the loss of weight of the lead compound during the reaction, to find out if it corresponds to the theoretical decrease in weight when diplumbic arsenates is converted into the compound,  $\text{Pb}_5\text{OH}(\text{AsO}_4)_3$ . The results of that determination show that it is not a hydrated compound, which is substantiated by the results of the arsenic determination. The formula may be written  $3\text{Pb}_3(\text{AsO}_4)_2 \cdot \text{Pb}(\text{OH})_2$ , which would indicate that it is a tritri-plumbic lead hydroxyarsenate but the formula  $\text{Pb}_5\text{OH}(\text{AsO}_4)_3$  is preferred and the compound will be referred to in this paper as the lead hydroxyarsenate. The com-

<sup>1</sup> Calculated from the factor 7.6034.

<sup>2</sup> The average of four samples.



pound occurs as a fine amorphous powder and does not show any definite structure when seen under the microscope.

**Preparation of the Sodium Compounds.**—Disodium arsenate occurs as two well-defined salts, which are generally represented, respectively, by the formulas  $\text{Na}_2\text{HAsO}_4 \cdot 12\text{H}_2\text{O}$  and  $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ . The compound  $\text{Na}_2\text{HAsO}_4 \cdot 12\text{H}_2\text{O}$  crystallizes out of solution of disodium arsenate at low temperatures and is efflorescent. The compound  $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$  crystallizes out of solution of disodium arsenate at temperatures above  $18^\circ$  and is not efflorescent.<sup>1</sup>

Samples of both these salts were prepared. Disodium arsenate is prepared commercially in the presence of an excess of sodium carbonate, and the salt, as it is put onto the market, is generally alkaline.

The crystals of  $\text{Na}_2\text{HAsO}_4 \cdot 12\text{H}_2\text{O}$  were prepared by saturating a solution at  $0^\circ$  with the fairly pure disodium arsenate and then adding a small amount of arsenic acid until the solution was neutral to phenolphthalein. During the crystallization the solution was kept at a low temperature. The crystals obtained in this manner were further purified by recrystallization three or four times, the precaution being taken not to use heat to dissolve the crystals. The crystals obtained in this manner were efflorescent and were only slightly alkaline with phenolphthalein.

The crystals of  $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$  were prepared by taking part of the solution that had been neutralized for the production of the crystals  $\text{Na}_2\text{HAsO}_4 \cdot 12\text{H}_2\text{O}$ , heating the solution to boiling and allowing the salt to crystallize from the warm solution and then recrystallize from warm solutions. The crystals obtained in this manner were not efflorescent and were decidedly alkaline with phenolphthalein.

Sodium nitrate, sodium acetate and sodium baborate were prepared by recrystallization of the so-called pure commercial salts.

**The Reaction of Diplumbic Arsenate with Sodium Baborate.**—The reaction of diplumbic arsenate with sodium baborate was examined, using the sample of diplumbic arsenate that had been isolated from all other compounds. The lead arsenate and the solution of sodium baborate were shaken intermittently for two days and then filtered. The soluble arsenic in the filtrate and the loss of weight of the lead compound were determined.

TABLE II.

	Vol. of soln. (Cc.).	% arsenic soluble.	Loss of wt. of lead compd. (%).	Sol. As calc. as $\text{H}_2\text{As}_2\text{O}_7$ . (%).	Sol. As calc. as $\text{H}_2\text{AsO}_4$ . (%).
1 g. $\text{PbHAsO}_4$ .....	500	37.15	14.28	14.23	15.19
5 g. Sodium baborate.....					
1 g. $\text{PbHAsO}_4$ .....	500	37.8	14.56	14.49	15.46
5 g. Sodium baborate.....					

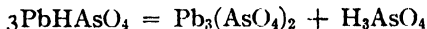
<sup>1</sup> Fresenius, *J. prakt. Chem.*, 56, 30.

When sodium silicate and the sodium compounds of the higher fatty acids were used very similar results were obtained. With the latter compounds, when the diplumbic arsenate was added in excess the fatty acids were precipitated.

When diplumbic arsenate is converted into lead hydroxyarsenate, pyroarsenic acid ( $\text{H}_4\text{As}_2\text{O}_7$ ) is eliminated from the lead compounds, which corresponds to 40% of the arsenic of the diplumbic arsenate and can be represented by the following:



If diplumbic arsenate should be converted into triplumbic arsenate, orthoarsenic acid ( $\text{H}_3\text{AsO}_4$ ) is eliminated from the lead compounds, which corresponds to 33.33% of the arsenic of the diplumbic arsenate and can be represented thus:



The above results then show:

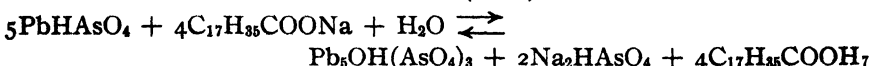
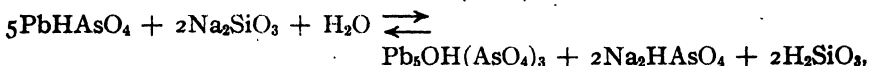
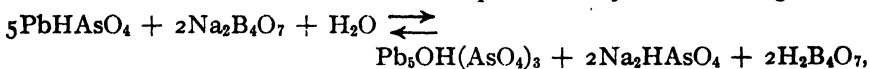
(1) That the diplumbic arsenate has been converted into lead hydroxyarsenate.

(2) That when diplumbic arsenate is converted into lead hydroxyarsenate, 40% of the arsenic of diplumbic arsenate has changed to a soluble arsenic compound as has been previously demonstrated.

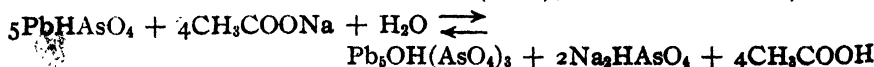
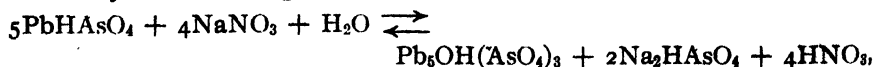
(3) That a free acid has been formed.

It will be demonstrated later that the ratio of the soluble arsenic to the free acid approaches one  $\text{HAsO}_4$  to two H.

Thus it can be inferred that the reactions of diplumbic arsenate with the sodium salts of weak acids can be represented by the following:



In each of the three reactions given above, the free acid is to a great extent thrown out of solution or has a very low degree of dissociation, therefore the reactions tend towards completion in that direction. Naturally the next step would be to study the reactions of diplumbic arsenate with sodium nitrate and sodium acetate, which are by products in the manufacture of lead arsenate. Then the reactions to be studied can be represented by the following:



The results of Tartar and Robinson indicate that lead arsenate prepared from aqueous solutions is a mixture of diplumbic arsenate and lead hydroxyarsenate, which is corroborated by the results obtained in the examination of the reaction of diplumbic arsenate with sodium biphosphate, and by other results which will be brought forward later; therefore, if a definite point of equilibrium could be established in the above systems, the products of the reactions of lead nitrate and lead acetate with disodium arsenate could accurately be defined as when disodium arsenate is added in excess, the products of the reactions are identical with the components of the systems which are to be studied.

**Reaction of Lead Nitrate with Disodium Arsenate. Point of Equilibrium.**—The mixtures were placed in bottles which were then attached to a shaker and intermittently shaken for the period stated in the tables. After the shaking the mixtures were filtered and the soluble arsenic and acidity in aliquot parts of the filtrate were determined.

To ascertain if the composition of the lead arsenate, produced by the reaction of lead nitrate with disodium arsenate agreed with that calculated from the concentrations of the system when they had come to an equilibrium, unless otherwise stated, the solutions of lead nitrate and disodium arsenate were placed in a container and attached to a shaker and were shaken until the composition became constant.

TABLE III.

Temperature.	Initial concentrations.		Concentrations at equilibrium.		
	PbHAsO <sub>4</sub> . Mol.	NaNO <sub>3</sub> . Mol.	Period. Days.	HNO <sub>3</sub> . Mol.	Na <sub>2</sub> HAsO <sub>4</sub> . Mol.
10–16°.....	0.01	0.008	5	0.00004	0.0000175
	0.1	0.08	5	0.00004	0.0000175
	Pb <sub>2</sub> OH(AsO <sub>4</sub> ) <sub>2</sub> . Mol.	Na <sub>2</sub> HAsO <sub>4</sub> . Mol.	HNO <sub>3</sub> . Mol.		
10–16°.....	0.002	0.004	0.008	60	0.00005
	0.02	0.04	0.08	60	0.00005

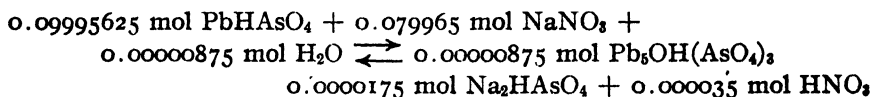
It was noted that the amounts of the concentration of HAsO<sub>4</sub> to the concentration of H<sup>+</sup> were approximately in the proportion of 1 to 2. With varying conditions there was a wide variation from this ratio, the variation being constant under similar conditions. As a study of the equation shows that the amount of soluble arsenic accurately defines the progress of the reaction, and as it can be more accurately determined than the acidity, the results of the soluble arsenic determination were adopted to designate the point of equilibrium when it was approached from PbHAsO<sub>4</sub> and NaNO<sub>3</sub>. The possibility of error being introduced into the system with these samples was also practically *nil*.

When the equilibrium was approached from Pb<sub>2</sub>OH(AsO<sub>4</sub>)<sub>2</sub>, Na<sub>2</sub>HAsO<sub>4</sub> and HNO<sub>3</sub>, as the large amount of soluble arsenic introduced into the system was reduced to a low concentration, the experimental error in its

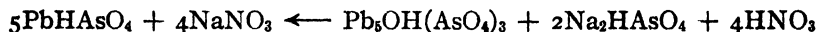
determination was greatly multiplied. And as the acidity gave constant results, then, when the concentration of the acid approached within experimental error of the concentration of the acid, when the equilibrium was approached from  $\text{PbHAsO}_4$  and  $\text{NaNO}_3$ , it was assumed that the systems had come to an equilibrium.

When the equilibrium was approached from  $\text{PbHAsO}_4$  and  $\text{NaNO}_3$ , constant results could readily be obtained and the system came to an equilibrium in a relatively short period; but when it was approached from  $\text{Pb}_5\text{OH}(\text{AsO}_4)_3$ ,  $\text{Na}_2\text{HAsO}_4$  and  $\text{HNO}_3$ , the rate of reaction was extremely slow. This was probably due to the physical condition of the lead hydroxyarsenate. That this is a factor will be apparent when the "Progress of the Reaction" is discussed. It was very difficult to obtain corroborative results and it was only after each component was thoroughly examined that constant results could be obtained.

The above results show that the following equation represents the concentrations of the components of the system when it has arrived at an equilibrium at stated concentration and temperature:

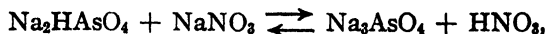


**The Effect of the Concentration of the Disodium Arsenate on the Equilibrium.**—The influence of increasing the concentration of disodium arsenate would be to move the equilibrium in the direction



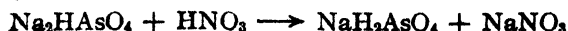
and, therefore, there would be a tendency to produce more diplumbic arsenate. If the disodium arsenate does function in this manner then the effect is masked by other influences.

If, in the presence of an excess of disodium arsenate in the system, lead nitrate is added, if the excess is only slight, the lead compounds of the arsenic acids are distributed in practically the same ratio as the other lead compounds of the system; from this it might be inferred that the sodium compounds were in an equilibrium which can be represented thus:



in which case, under certain conditions, the effect of the concentration of the disodium arsenate would be an effect of a much lower order than its mass action.

The compounds,  $\text{Na}_3\text{AsO}_4$ ,  $\text{Na}_2\text{HAsO}_4$  and  $\text{NaH}_2\text{AsO}_4$ , are all alkaline to congo red and methyl orange and these indicators can be used to indicate the completion of the following reaction at low temperatures:



If solutions of disodium arsenate are made strongly acid, using either

of these two indicators, and are then heated, they become decidedly alkaline, and when cooled, become acid again.

It is not intended in this paper to make a detailed examination of the movable equilibrium of the sodium compounds, but this phenomenon has been mentioned because it can be readily seen that it will give an insight into the influence of disodium arsenate upon the equilibrium and upon the products of the reaction of lead nitrate and disodium arsenate.

While it was found that a slight excess of neutral disodium arsenate did not affect the equilibrium, yet a slight excess of solutions of the compound  $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$  always moved the equilibrium in the direction



The system must produce more acid to neutralize the alkalinity of the disodium arsenate before it can proceed to an equilibrium; therefore, more lead hydroxyarsenate would be produced.

TABLE IV.

Composition of Lead Arsenates.

	$\text{As}_2\text{O}_5$
Prepared from 0.1 mol $\text{Pb}(\text{NO}_3)_2$ and 0.1 mol $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ ...	33.08
Prepared from 0.1 mol $\text{Pb}(\text{NO}_3)_2$ and 0.2 mol $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ ...	32.00

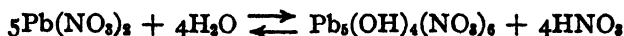
These results disproved the contention of Holland and Reed<sup>1</sup> that the influence of an excess of the alkaline disodium arsenate ( $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ ) would be to produce a compound approaching nearer to the theoretical composition of diplumbic arsenate.

It is worthy of note that while the alkalinity of the excess of disodium arsenate exerts such an influence on the equilibrium and on the composition of lead arsenate, yet the effect of the alkalinity is not apparent when the arsenate is completely precipitated. This may be due to the alkalinity being neutralized by the acidity of the lead nitrate solution or to the distribution of the arsenic acids before and after precipitation.

**The Effect of the Concentration of the Lead Nitrate on the Reaction.**—The methods by which the point of equilibrium was established cannot be used when there is an excess of lead nitrate, as the soluble arsenic is eliminated and general acidimetric methods are not applicable in the presence of the lead compound. From the arsenic content of the resulting lead arsenates the point of equilibrium could be established, but that would not be very satisfactory, as it is possible that the limit of error in the determination of the arsenic content might be greater than the influence of the lead nitrate.

A probable indication of the influence of the lead nitrate upon the reaction might be obtained from a study of the solution of the compound. When lead nitrate is dissolved in dilute solutions there is a turbidity and the solution becomes acid; this is due to hydrolysis, which may be represented in part by the following:

<sup>1</sup> Mass. Agr. Exp. Sta., 24th Ann. Report, p. 201.



As none of the general titration methods can be used to determine the acidity of the lead nitrate solution, a rather crude colorimetric method was employed to obtain a rough approximation of the acidity of the solution. Strips of litmus paper were dipped, for a short interval, simultaneously into lead nitrate solutions and acid solutions of known strength. The acidity of the solution being fairly great, an excess would tend to produce more diplumbic arsenate but a measure of the acidity is also a measure of the amount of the hydroxy compound. The tendency of this hydroxy compound would be to produce more lead hydroxyarsenate, thus an excess of lead nitrate solution exerts two influences which are directly opposed to each other. Each may offset the effect of the other, in which case an excess of lead nitrate would not affect the composition of the precipitate.

### The Effect of Concentration and Temperature on the Equilibrium.

TABLE V.

The Initial and Final Concentrations of the System at Different Temperatures and Concentrations.

Temperature.	Initial concentrations.		Period.	Concentrations at equilibrium.	
	PbHAsO <sub>4</sub> . Mol.	NaNO <sub>3</sub> . Mol.		HNO <sub>3</sub> . Mol.	Na <sub>2</sub> HAsO <sub>4</sub> . Mol.
10-16° .....	0.01	0.2	5 days	0.00004	0.0000175
	0.01	0.02	5 days	0.00004	0.0000175
19-23° .....	0.01	0.2	5 days	0.00011	0.00007
	0.01	0.02	5 days	0.00011	0.00007
Boiling; Barometric pressure, 637 mm. <sup>1</sup> .....	0.01	0.2	8 hrs.	0.000575	0.000525
	0.01	0.02	8 hrs.	0.00045	0.000425

TABLE VI.

Composition of Lead Arsenate Produced at Different Concentrations and Temperatures.

Temperature.	Concentration of reacting compounds.	Calculated.		Found. Arsenic as As <sub>2</sub> O <sub>3</sub> .
		Lead as PbO.	Arsenic as As <sub>2</sub> O <sub>3</sub> .	
10-16° .....	0.1	64.296	33.11	33.08
	0.01	64.331	33.076	33.05
19-23° .....	0.1	64.309	33.091	33.05
	0.01	64.46	32.886	32.9
Boiling; Barometric pressure, 638 mm. ....	0.1	64.421	33.006	32.95
	0.01	65.355	32.26	32.32

As the solubilities of diplumbic arsenate and lead hydroxyarsenate are only very slight, as long as these compounds are in contact with the solution, their active masses can be considered constant. Therefore, an in-

<sup>1</sup> The altitude of the Chemistry laboratory of the Montana Experiment Station is 4910 feet above sea level.

crease in the amounts of the lead arsenates in the system would not affect the equilibrium.

An increase in the concentration of the sodium nitrate would be expected to move the equilibrium in the direction



At low temperatures, although the concentration of the sodium nitrate was increased ten and one hundred fold, there was the same amount of soluble arsenic produced. It is probable that the influence of a variation in the concentration of the sodium nitrate at low temperatures is so slight that it cannot be detected by the methods used. The results show that as the temperature rises the influence of a variation in the concentration of the sodium nitrate becomes apparent.

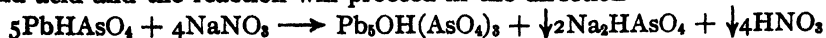
In the production of lead arsenate, when the reaction has come to an equilibrium, as the concentration increases, the relative amount of lead hydroxyarsenate will decrease. Therefore, as the concentration increases the composition of the resulting lead arsenate will approach nearer to the theoretical composition of diplumbic arsenate. This is not in accord with the deductions of other investigators. The error in their conception was due to the fact that the products of the reaction were not allowed to come to an equilibrium, and that the progress of the reaction in dilute solutions, within certain limits, is faster than in the more concentrated.

As the temperature rises the equilibrium moves in the direction



and more lead hydroxyarsenate is formed; therefore, as the temperature rises the composition of the resulting lead arsenate will recede from the theoretical composition of diplumbic arsenate. There are probably two factors that cause the movement of the equilibrium Pt: the depression of the dissociation of the acid and the tendency of the sodium compounds of the system to become more alkaline as the temperature rises.

**The Effect of Washing Away the Soluble Products.**—In Table VI the calculated compositions of the precipitates at different concentrations are given, which represent the compositions of the precipitates as they exist before they have been isolated from the soluble products of the reactions. The results have shown that when the concentration of the sodium nitrate is decreased the systems attain to the same concentrations of soluble arsenic and acid. After each removal and addition of the washing fluid the concentrations of soluble arsenic and acid have been greatly reduced. Therefore, as the concentration of sodium nitrate still remains relatively great, the system will tend to produce more soluble arsenic and acid and the reaction will proceed in the direction



and more lead hydroxyarsenate will be formed which will be proportional to the rate at which the concentration of the sodium nitrate is reduced

by the removal of the washing fluid. While the increased amount of lead hydroxyarsenate produced is comparatively small, yet it is sufficient to materially alter the composition of the precipitate. It would probably be an economic advantage to use a slightly acidulated water as the washing fluid in the commercial production of lead arsenate. There is a loss of disodium arsenate by each addition of the washing fluid when distilled water is used. This loss is greatly multiplied on account of the general alkalinity of the average water supply. If sufficient nitric acid were added to neutralize the alkalinity of the water and leave a slightly acid solution, the loss of soluble arsenic would be reduced to a minimum.

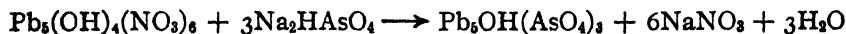
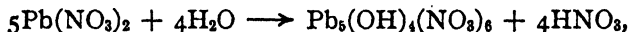
**Progress of the Reaction.**—Various investigators claim that the reaction between lead nitrate and disodium arsenate takes place as represented by the equation



and some have added that a same amount of the tribasic arsenate is formed due to a secondary reaction. While this equation, to a certain extent, represents the initial and final stages, it does not represent the reaction as it actually takes place.

It has been pointed out that diplumbic arsenate occurs in comparatively large crystalline plates and that lead hydroxyarsenate is a very fine amorphous precipitate. When solutions of lead nitrate and disodium arsenate are mixed, the precipitate as it first appears is extremely fine and then quickly changes to a relatively large flocculent crystalline precipitate. The transformation is too rapid to be a physical change due to the growth of the crystal by solution, as the diplumbic arsenate is only very slightly soluble. While the precipitate clings together, a microscopic examination shows that the change is not due to the coagulating power of sodium nitrate. It is contended that there has been a reaction between the precipitate and the solution and that the compound which is precipitated is lead hydroxyarsenate which reacts with disodium arsenate and the nitric acid of the solution, the reaction proceeding to an equilibrium, as in the system that has been studied.

The course of the reaction between lead nitrate and disodium arsenate can probably be represented by the following:



Attempts were made to regulate the progress of the reaction. If the influence of the action of the solution upon the precipitate could be retarded then it might be possible to isolate the precipitate in an initial stage of the reaction. When the precipitates were produced at infinite dilutions (under 0.001) and the solution decanted as soon as the pre-



precipitate had settled, then washed and dried, it was found that the precipitates were composed practically of pure lead hydroxyarsenate.

TABLE VII.

Composition of Precipitate from Lead Nitrate and Disodium Arsenate at Infinite Dilution.

	Lead as PbO.	Arsenic as $\text{As}_2\text{O}_5$ .
Sample 1.....	74.6	23.52
Sample 2.....	74.2	23.94

Although the progress of the reaction is rapid in the concentrated solutions, it was found that in infinitely dilute solutions the progress was extremely slow. This is probably due to the condition of the lead hydroxyarsenate, which might account for the slow rate of reaction when the equilibrium was approached from  $\text{PbOH}(\text{AsO}_4)_3 \cdot 2\text{Na}_2\text{HAsO}_4$  and  $4\text{HNO}_3$ .

When the attempt was made to isolate diplumbic arsenate it was thought advisable to avoid the production of lead hydroxyarsenate in such a condition that it would not be readily acted upon by the solution. As it seemed probable that this might occur if it was endeavored to prepare diplumbic arsenate by re-precipitating with ammonium hydroxide, lead arsenate that had been dissolved with nitric acid, as suggested by Tartar and Robinson, the previously mentioned modification was adopted.

**The Reaction of Lead Acetate with Disodium Arsenate.**—The same methods as were used in the examination of the reaction of lead nitrate with disodium arsenate were employed to examine the reaction of lead acetate with disodium arsenate.

TABLE VIII.

Temperature.	Initial concentrations. (Mol).		Period.	Concentrations at equilibrium. (Mol).	
	$\text{PbHAsO}_4$ .	$\text{CH}_3\text{COONa}$ .		$\text{CH}_3\text{COOH}$ .	$\text{Na}_2\text{HAsO}_4$ .
15-22°.....	0.01	0.008	10 days	0.00016	0.000065
	0.01	0.02	10 days	0.00022	0.0000738
	0.01	0.2	10 days	0.00108	0.00053
Boiling; Bar. press.					
633 mm.....	0.01	0.2	8 hrs.	0.0056	0.00275
	$\text{Pb}_2\text{OH}(\text{AsO}_4)_3$ .	$\text{Na}_2\text{H}_2\text{AsO}_4$ .		$\text{CH}_3\text{COOH}$ .	
15-22°.....	0.002	0.004	0.008	6 mos.	0.00012

TABLE IX.

Composition of Lead Arsenates Produced by the Reaction of Lead Acetate with Disodium Arsenate at Different Concentrations and Temperatures.

Temperature.	Concentration of reacting compounds.	Composition.				
		Calculated.		Found. Soluble products removed.		
		Lead as PbO.	Arsenic as $\text{As}_2\text{O}_5$ .	Immediately. Arsenic as $\text{As}_2\text{O}_5$ .	After two weeks. Arsenic as $\text{As}_2\text{O}_5$ .	After two months. Arsenic as $\text{As}_2\text{O}_5$ .
15-22°.....	0.01	64.47	32.95	24.5	31.52	31.74
	0.1	64.42	32.00	24.5	30.75	31.92
Boiling; Bar. press. 633 mm.	0.1	64.97	32.54	30.5 <sup>1</sup>	...	...

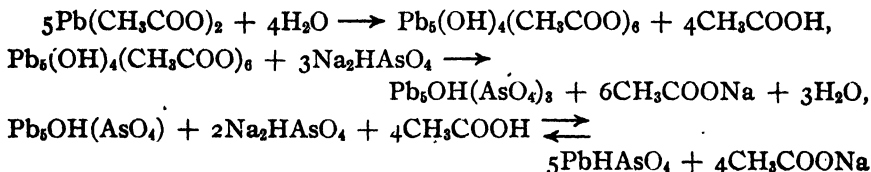
<sup>1</sup> After being boiled for eight hours under reflux condenser.

TABLE X.

The Composition of Lead Arsenate from Lead Acetate and Disodium Arsenate at Infinite Dilution.

	Lead as PbO.	Arsenic as $\text{As}_2\text{O}_3$ .
Sample No. 1.....	74.9	23.26
Sample No. 2.....	74.3	23.9

These results show that the progress of the reaction of lead acetate with disodium arsenate is similar to the progress of the reaction of lead nitrate with disodium arsenate and can be represented by the following:



The results also show that, when the reaction of lead acetate with disodium arsenate has come to an equilibrium, the resulting lead arsenate is composed principally of diplumbic arsenate. As the reaction of lead acetate with disodium arsenate has been employed so extensively for the commercial production of lead arsenate and has also been studied by numerous investigators, it appears to be remarkable that the fact has been so completely overlooked that there was a reaction between the precipitate as it was formed and the solution. Haywood and McConnell<sup>1</sup> appear to be the only investigators that have found it was possible to produce a lead arsenate by the reaction of lead acetate with disodium arsenate that was composed principally of diplumbic arsenate, though they make no mention of how their results were obtained.

There has been no attempt in this paper to derive the equilibrium constants. Before these can be obtained with any degree of accuracy it will probably be necessary to make a more thorough examination of the influence of the sodium compounds on the equilibrium and also to attain the point of equilibrium of the systems within a narrower range of temperature than has been attempted in this investigation.

### Conclusions.

In the reactions of lead nitrate and lead acetate with disodium arsenate:

The lead arsenates produced are mixtures of diplumbic arsenate,  $\text{PbHAsO}_4$ , and lead hydroxyarsenate,  $\text{Pb}_5\text{OH}(\text{AsO}_4)_3$ .

The products of the reactions at low temperatures, when the reactions have come to an equilibrium, whether lead acetate or lead nitrate is used, consist principally of diplumbic arsenate.

The products of the reactions at infinite dilutions (less than 0.001 mol) whether lead acetate or lead nitrate is used, consist principally

<sup>1</sup> U. S. Dept. Agr., Bur. Chem., *Bull.* 131.

of lead hydroxyarsenate if the precipitates are filtered immediately after the precipitation.

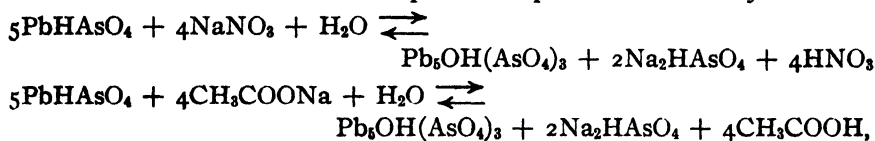
The precipitate that is first formed is lead hydroxyarsenate; diplumbic arsenate is produced by a secondary reaction.

As the excess of the alkaline disodium arsenate increases greater amounts of lead hydroxyarsenate are produced.

As the concentration increases, when the reactions have come to an equilibrium, the relative amount of diplumbic arsenate increases.

As the temperature rises more lead hydroxyarsenate is formed.

From the determination of the point of equilibrium in the systems



the composition of the resulting lead arsenate of the respective reactions can be calculated.

BOZEMAN, MONT.

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[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, OF THE U. S. DEPARTMENT OF AGRICULTURE.]

## THE ARSENATES OF LEAD.

[FIRST PAPER.]

By C. C. McDONNELL AND C. M. SMITH.

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Arsenate of lead, until comparatively recent years, was of no commercial importance; however, since it was first recommended as an insecticide,<sup>1</sup> it has come into very extensive use, and several thousand tons are used annually for the destruction of certain leaf-eating insects. Fourteen U. S. patents<sup>2</sup> relating to commercial processes for its production have been issued. Despite its large and increasing use and importance, the chemical and physical properties of the several arsenates of lead have not been very thoroughly investigated. Most of the recent work has been directed toward determining what products result from the reaction between lead nitrate or lead acetate, and disodium hydrogen arsenate,  $\text{Na}_2\text{HAsO}_4$ , which compounds have been widely recommended for its preparation for spraying purposes.

The references in the literature concerning the preparation and properties of the arsenates of lead are based mostly upon the work of the earlier chemists, Berzelius, Mitscherlich, Wittstein, Graham, H. Rose, and Salkowski, whose conclusions are somewhat contradictory, and

<sup>1</sup> Report Mass. Board of Agr., 1893, p. 282.

<sup>2</sup> Nos. 870,915, 892,603, 903,389, 929,952, 1,014,742, 1,056,340, 1,064,023, 1,064,639, 1,100,673, 1,100,686, 1,141,920, 1,169,114, 1,172,741, 1,175,565.

frequently misquoted by more recent writers. The latter condition has been due in part no doubt to changes in nomenclature.

The older investigators recognized "neutral" lead arsenate (which term was applied indiscriminately to both dilead orthoarsenate and lead pyroarsenate) and "basic" or "sub" arsenate (later designated trilead arsenate). The naturally occurring mineral now known as mimetite was for many years regarded as "sub" arsenate of lead until the researches of V. Rose<sup>1</sup> and Wöhler<sup>2</sup> showed it to be lead chloroarsenate of the formula  $\text{Pb}_4(\text{PbCl})(\text{AsO}_4)_3$ .

The work of the more recent investigators will be considered under the several subheadings.

Arsenic acid, as is well known, forms several distinct classes of salts—orthoarsenates, derived from orthoarsenic acid,  $\text{H}_3\text{AsO}_4$ , which are subdivided into mono-, di- and tri-metallic salts; pyroarsenates, derived from pyroarsenic acid,  $\text{H}_4\text{As}_2\text{O}_7$ ; and metarsenates, derived from metarsenic acid,  $\text{HAsO}_3$ .

Representatives of all of these classes are found among the various metallic arsenates, and, theoretically, lead should also form corresponding compounds.

**Monolead Orthoarsenate**,  $\text{PbH}_4(\text{AsO}_4)_2$ .—One might naturally suppose that monolead arsenate would result from the interaction of solutions of lead nitrate or acetate and a monoalkali arsenate, such as potassium dihydrogen arsenate,  $\text{KH}_2\text{AsO}_4$ .<sup>3</sup> However, this does not occur, at least at moderate dilutions. Under such conditions we invariably obtained dilead arsenate,  $\text{PbHAsO}_4$ , with simultaneous liberation of free acid in the solution, according to the following equation:



Likewise, dilead arsenate is formed when arsenic acid is permitted to react with lead nitrate at ordinary dilutions. These facts suggested that monolead arsenate is unstable in moderately acid media, but might exist at higher acid concentrations. When 20 g. of dilead arsenate were boiled for two hours with 50% arsenic acid and the liquid filtered off, the latter was found to contain but a trace of lead, and the residue, after washing with 95% alcohol (in which arsenic acid is readily soluble), was found to have been practically unchanged. When the arsenic acid concentration was raised to 86%  $\text{H}_3\text{AsO}_4$ , transposition took place. 400 g. of 86% arsenic acid were brought to boiling (about 130 °), and pure dilead arsenate was added in successive small portions. The first few additions dissolved completely, and 7 g. went into solution before a permanent

<sup>1</sup> *Neues Allgemeines Journal der Chemie*, 3, 65 (1804).

<sup>2</sup> *Ann. Phys. Chem.*, 4, 161 (1825).

<sup>3</sup> Commercial potassium arsenate is the dihydrogen salt,  $\text{KH}_2\text{AsO}_4$ , although frequently labeled  $\text{K}_2\text{HAsO}_4$ .

residue remained. A total of 10 g. was added and the heating continued for several minutes. The solution was then filtered through asbestos and allowed to stand until cold, when a bulky mass of moderate sized crystals had deposited. They were separated from the mother liquor as well as possible by centrifuging, then washed with absolute alcohol and dried at  $110^{\circ}$ . Analysis showed this compound to be monolead orthoarsenate (a).

By the addition of a small amount of nitric acid to the boiling arsenic acid solution a larger yield of this material may be obtained. One such experiment, using a solution containing 86% arsenic acid and 2% nitric acid, gave a product of almost theoretical composition (b).

	Found. (a).	Found. (b).	Calc. for $\text{PbH}_4(\text{AsO}_4)_2$ .
Lead oxide, $\text{PbO}$ .....	45.03%	45.59%	45.62%
Arsenic oxide, $\text{As}_2\text{O}_5$ .....	47.42	47.14	47.01
Water of constitution (by ignition).....	7.55	7.34	7.37
	100.00	100.07	100.00

The concentration at which the change from di- to monolead arsenate takes place was determined approximately by using arsenic acid of various concentrations. It was found that 93, 91, 88 and 86%  $\text{H}_3\text{AsO}_4$  deposited monolead arsenate, while concentrations of 80%  $\text{H}_3\text{AsO}_4$ , or less, gave dilead arsenate, showing that the transition concentration lies somewhere between 80 and 86% arsenic acid.

*Properties.*—Under the microscope the monolead arsenate prepared as described was seen to consist entirely of long, narrow, rhomboidal plates. The acute angle at the end is  $68^{\circ}$  (measured by rotating stage). They are biaxial, probably negative, and extinguish at an angle of  $8^{\circ}$  with reference to the longer edge. The minimum index of refraction, normal to the face upon which the crystals naturally lie, is about 1.75, and the birefringence is very strong. (These results indicate that they are mono- or triclinic, probably the latter, as the normal to the crystal did not coincide with any one of the three ether axes.)

The specific gravity, determined on 2.5 g. of material, using a 25 cc. specific gravity bottle and benzene as the liquid, was found to be 4.46 at  $15^{\circ}$  compared with water at the same temperature.

Chemically, monolead arsenate is very unstable. In contact with water it gives up arsenic acid immediately; 0.5 g. treated with 100 cc. of water for 3 hours at room temperature gave 21.89% soluble  $\text{As}_2\text{O}_5$ . The same proportions boiled for 5 minutes gave 22.91% soluble  $\text{As}_2\text{O}_5$ . The lead dissolved was practically *nil* in both cases, showing that water causes complete decomposition of monolead arsenate into dilead arsenate and arsenic acid. The crystals which had been treated with water retained their shape, as shown by microscopical examination, but were almost

without exception of a brown color, and nearly opaque, with the appearance of having been fractured throughout.

Monolead arsenate, when heated very slowly, begins to lose water at  $140^{\circ}$ . Heated at  $150^{\circ}$  for 7 hours it lost approximately one half its total content, corresponding to one molecule of water. Upon further heating at this temperature it continued to lose weight slowly, but the entire theoretical amount was not lost after heating 5 hours a day for three successive days, nor after three additional 5-hour periods at  $210^{\circ}$ . Total loss during this heating, 6.83%. When heated over a low flame below redness it lost 7.34% (theory for water of constitution, 7.37%). Heated to fusion it was partially reduced and lost  $\text{As}_2\text{O}_3$ , which could be seen escaping from the crucible.

**Dilead Orthoarsenate,  $\text{PbHAsO}_4$ .**—The material derived from orthoarsenic acid by the replacement of two of the hydrogen atoms by lead has been known by various names, such as neutral lead arsenate, acid lead arsenate, bibasic lead arsenate, lead hydrogen arsenate, diplumbic hydrogen arsenate, diplumbic arsenate, and simply lead arsenate. It would seem that dilead arsenate is sufficiently specific; in fact, in commercial usage when the term "lead arsenate" is used it is generally this compound that is meant. It is by far the most important arsenate of lead. The formula may be expressed as  $\text{Pb}_2\text{H}_2(\text{AsO}_4)_2$ , or, since its molecular weight is not known, simply  $\text{PbHAsO}_4$ .

There are numerous references in the literature to the preparation and properties of this material. They are, however, in some cases, contradictory.

Berzelius (*Neues Journal für Chemie und Physik*, 23, 174 (1819); *Ann. chim. phys.*, [2] 11, 229 (1819)) states that it is produced when a solution of nitrate of lead is added to a solution of arsenate of soda with the precaution that the whole amount of the arsenic acid be not precipitated, and describes the product (*Lehrbuch der Chemie*, 3, 72 (1845)) as a white powder, insoluble in water, soluble in  $\text{HCl}$  and  $\text{HNO}_3$ , melting at white heat to an opaque yellowish mass.

Mitscherlich (*Ann. chim. phys.*, 19, 368 (1821)).—Lead acetate completely decomposes the bin-arsenates ( $\text{M}'\text{H}_2\text{AsO}_4$ ), for the arsenate of lead is insoluble in acetic acid. The precipitate is ordinarily the neutral salt (dilead arsenate), but one can never be sure that the neutral salt is not mixed with the sub-salt (trilead arsenate). Distinguished from the sub-salt by melting easily and crystallizing on cooling.

Wittstein, "Entymologisch Chemisches Handwörterbuch," 2, 929 (1847).—Neutral lead arsenate precipitates as a white insoluble powder when lead acetate is mixed with neutral arsenates of the alkalis. It melts at white heat to a yellow non-transparent glass.

H. Rose, "Ausführliches Handbuch der Analytischen Chemie," 1, 381 (1851).—A solution of nitrate or acetate of lead produces in solutions of arsenic acid, or alkali arsenates, an immediate white precipitate of lead arsenate, soluble in nitric, insoluble in acetic acid; does not crystallize when melted before the blowpipe. In certain cases the lead arsenate may contain more lead and be, therefore, more basic (*Ibid.*, 2, 406).

Gmelin, "Handbook of Chemistry," trans. by Watts, 5, 173 (1851).—It is formed by the slow action of arsenic acid and air upon metallic lead; also by the precipitation of lead chloride with arsenic acid. Soluble in hydrochloric acid.

Salkowski, *J. prakt. Chem.*, 104, 160 (1868).—Produced by the addition of neutral sodium arsenate to lead acetate as long as a precipitate forms. Crystalline. Converted to lead pyroarsenate upon ignition.

Duvillier, *Compt. rend.*, 81, 1251 (1875).—If a boiling solution of arsenate of lead in nitric acid be diluted with water it quickly deposits little plates of dilead arsenate.

Goguel, "Mémoires de la Société des Sciences Physiques et Naturelles de Bordeaux," Ser. [5] 1, 135 (1896).—By the addition of concentrated arsenic acid to a boiling solution of lead nitrate containing about 1% nitric acid obtained crystals in micaceous leaflets, unctuous to the touch, insoluble in water, soluble in dilute nitric acid; water of constitution lost above 200°; not further decomposed at red heat. Optical measurements of the crystals showed them to belong to the monoclinic system.

De Schulten, *Bulletin de la Société Française de Mineralogie*, 27, No. 6, 113 (1904).—Well formed monoclinic crystals of dilead arsenate were obtained by the slow addition of a 0.3% solution of ammonia to a hot nitric acid solution of lead arsenate. Sp. gr. 6.076 at 15°. Optical and goniometric measurements are given.

Holland and Reed (Mass. Agr. Expt. Station, 24th Ann. Report, Part I, 204 (1912)) state that acid lead arsenate of theoretical composition is readily prepared from nitrate of lead and sodium arsenate, provided dilute solutions are employed and the sodium salt added carefully in excess (10%).

Tartar and Robinson (THIS JOURNAL, 36, 1846 (1914)).—Pure dilead arsenate was obtained as a white amorphous powder by the addition of dilute ammonia, with constant stirring, to a saturated solution of lead arsenate in nitric acid until three-fourths of the nitric acid used was neutralized. Sp. gr. 5.786.

The most frequently quoted method for the production of dilead orthoarsenate is the reaction between solutions of lead acetate, or nitrate, and the "neutral" arsenate of soda,  $\text{Na}_2\text{HAsO}_4$ . R. E. Curry and T. O. Smith,<sup>1</sup> after a phase rule study, conclude that "in the system disodium hydrogen arsenate, lead nitrate and water there exists at 25° only one compound, lead hydrogen arsenate;" however, F. J. Smith,<sup>2</sup> Pickering<sup>3</sup> Haywood<sup>4</sup> and Tartar and Robinson<sup>5</sup> have noted that the action between lead nitrate and disodium arsenate is not constant, resulting in a product usually slightly more basic than dilead arsenate. Experiments made by us are in agreement with the latter view. (It should be noted that Curry and Smith worked with very dilute solutions.) Using lead acetate and disodium arsenate in suitable proportions we have obtained a material even more basic than trilead arsenate.

Mitscherlich used as his source of arsenic the "binarsenates" of ammonia, soda, and potash, by which he meant salts of the type  $\text{M}'\text{H}_2\text{AsO}_4$ , and not those of the type  $\text{M}'_2\text{HAsO}_4$ , as is stated in several later quotations of his work. We have found that if lead nitrate or acetate in moderately

<sup>1</sup> THIS JOURNAL, 37, 1685 (1915).

<sup>2</sup> Mass. State Board of Agr., 45th Ann. Report, 357 (1897).

<sup>3</sup> J. Chem. Soc., 91, 310 (1907).

<sup>4</sup> Bur. Chem., Bull. 105, 165 (1907).

<sup>5</sup> Loc. cit.

strong solutions is precipitated by means of an excess of monopotassium arsenate, dilead arsenate is produced, which, when dried, is a very bulky, amorphous powder, of practically theoretical composition. The use of very dilute solutions results in the formation of a crystalline product having a silky appearance.

Arsenic acid in conjunction with lead acetate or nitrate, as stated by H. Rose, is as efficient as the method just described for making a pure product and the tendency to crystallization is greater owing to the greater acidity of the solution.

The few experiments made by us on the reaction between lead chloride and arsenic acid, gave, instead of dilead arsenate (which Gmelin states is so formed), a chloroarsenate approximating to natural mimetite,  $\text{Pb}_4(\text{PbCl})(\text{AsO}_4)_3$ , as we have shown in a previous paper.<sup>1</sup> It may be that under certain conditions dilead arsenate would also deposit from such solutions. In a number of experiments with saturated lead chloride and soluble arsenates (0.04 mol  $\text{As}_2\text{O}_5$  per l.), a lead chloroarsenate was always obtained, except that when a solution of lead chloride was added to potassium or sodium dihydrogen arsenate, the latter in excess, pure dilead arsenate was precipitated.

We first obtained crystals by placing a solution of cold dilute nitric acid, saturated with dilead arsenate, under a bell jar by the side of an open dish of concentrated ammonia. The slow absorption of the ammonia vapors neutralized the acid and precipitated dilead arsenate in the form of long, slender, glistening crystals. A pure crystalline product was also obtained by adding a dilute solution of ammonium acetate to a solution of dilead arsenate in boiling nitric acid. We found the method of Duvillier to be the most satisfactory for producing a pure crystallized compound, as it permits of successive recrystallizations. On pouring a solution of nitric acid (1 : 4) saturated at the boiling point with dilead arsenate into about six times its volume of boiling water, a mass of beautiful crystals separated, consisting of very thin plates of sufficient size to be visible to the eye. The analysis of this product gave results in practical accord with theory.

	Found.	Theory for $\text{Pb}_2\text{HAsO}_4$ .
Lead oxide, $\text{PbO}$ .....	64.20%	64.29%
Arsenic oxide, $\text{As}_2\text{O}_5$ .....	33.13%	33.13%
Water of constitution (by diff.).....	2.67%	2.58%
	<hr/> 100.00%	<hr/> 100.00%

When the nitric acid solution was allowed to cool without dilution a smaller crop of much larger crystals was obtained, some being as large as  $1 \times 1 \times 0.03$  mm.

*Properties.*—Goguel and de Schulten both described the product as occurring. *Am. J. Sci.*, [4] 42, 139 (1916).



curing in monoclinic leaflets, tabular parallel to the plane of symmetry, the latter containing the optic axes. The crystals in both cases had an acute angle of about  $84^\circ$ . Goguel states that extinction occurred at  $21-22^\circ$ , while de Schulten gives for this measurement  $38^\circ$ , both in reference to the obtuse angle of the crystal. Those prepared by us had an acute angle of  $85^\circ$  and extinguished at  $29^\circ$  within the obtuse angle. They are optically positive and the birefringence is quite high.

The determination of the density of two lots of dilead arsenate crystals, using a 10 cc. specific gravity bottle, 6 g. of material, and water<sup>1</sup> as the liquid, gave sp. gr. 15/15 6.042 and 6.053, agreeing with the value 6.076 as given by de Schulten. A determination made on 4.5 g. of amorphous material, using benzene as the liquid, gave sp. gr. 15/15 5.93. Tartar and Robinson<sup>2</sup> report a value of 5.786. (The results obtained on the crystalline compound are no doubt more nearly correct.)

Dilead arsenate is very little soluble in water; 5 g. boiled for 6 hours under a reflux condenser with 200 cc. of water gave but 4 mg. of  $\text{As}_2\text{O}_5$  in solution. Cold water has even less effect. Experiments being conducted by C. C. McDonnell and J. J. T. Graham (the results of which have not yet been published), show that long-continued exposure to constantly changing water brings about decomposition, both lead and arsenic dissolving, but the latter at a relatively greater rate, leaving the residue more basic than dilead arsenate.

Upon heating, dilead arsenate loses its water of constitution and is converted into the pyroarsenate. Experiments made by heating small portions at various constant temperatures in an air oven, showed that the temperature of conversion to pyroarsenate is within a few degrees of  $280^\circ$ . The material used in these tests did not lose its crystalline appearance. It melts at a bright red heat and on cooling crystallizes to lead pyroarsenate.

**Trilead Orthoarsenate,  $\text{Pb}_3(\text{AsO}_4)_2$ .**—It is stated by Berzelius<sup>3</sup> that trilead arsenate is formed by the action of ammonia on "neutral" lead arsenate ( $\text{PbHAsO}_4$ ), and<sup>4</sup> when a neutral arsenic acid salt ( $\text{M}'_2\text{HASO}_4$ ) is mixed with neutral lead acetate. Mitscherlich<sup>5</sup> says it is produced by the addition of neutral lead salts to a solution of an arsenate, the latter in excess; and<sup>6</sup> by the addition of lead acetate in excess to bi-arsenates ( $\text{M}'\text{H}_2\text{AsO}_4$ ), with subsequent boiling. Graham<sup>7</sup> claims to have produced it by the addition of lead acetate to subarsenate of soda ( $\text{Na}_3\text{AsO}_4$ ).

<sup>1</sup> The action of water on dilead arsenate is so slight that no error is here introduced.

<sup>2</sup> *Loc. cit.*, p. 1849.

<sup>3</sup> *Ann. chim. phys.*, [2] 11, 229 (1819).

<sup>4</sup> *Lehrbuch der Chemie*, 3, 72 (1845).

<sup>5</sup> *Ann. chim. phys.*, 19, 363 (1821).

<sup>6</sup> *Ibid.*, p. 368.

<sup>7</sup> *Philosoph. Trans. Royal Society*, 123, 266 (1833).

The double decomposition between soluble arsenates and lead salts has been used by a number of more recent investigators. Holland and Reed,<sup>1</sup> using disodium arsenate and lead acetate, obtained, under restricted conditions, a product containing lead and arsenic in the proper ratio for trilead arsenate. Tartar and Robinson,<sup>2</sup> however, state that pure trilead arsenate cannot be prepared by the reaction of these two compounds. Our work, as well as the observations of others, shows that the compound resulting from such reactions varies with changing conditions. In a series of experiments the reactions between the two lead salts, nitrate and acetate, and the two arsenates  $\text{Na}_2\text{HAsO}_4$  and  $\text{Na}_3\text{AsO}_4$  were studied, first with lead salt in excess and then with arsenate in excess, the concentrations employed being 0.4 mol  $\text{PbO}$  and  $\text{As}_2\text{O}_5$ , respectively, per liter. The results are here tabulated.

Salt in excess.	Precipitant.	Molecular ratio $\frac{\text{PbO}}{\text{in precipitate As}_2\text{O}_5}$
$\text{Pb}(\text{Ac})_2$	$\text{Na}_2\text{HAsO}_4$	3.29
$\text{Pb}(\text{Ac})_2$	$\text{Na}_3\text{AsO}_4$	3.36
$\text{Pb}(\text{NO}_3)_2$	$\text{Na}_2\text{HAsO}_4$	2.19
$\text{Pb}(\text{NO}_3)_2$	$\text{Na}_3\text{AsO}_4$	3.14
$\text{Na}_2\text{HAsO}_4$	$\text{Pb}(\text{Ac})_2$	2.96
$\text{Na}_2\text{HAsO}_4$	$\text{Pb}(\text{NO}_3)_2$	2.12
$\text{Na}_3\text{AsO}_4$	$\text{Pb}(\text{Ac})_2$	3.25
$\text{Na}_3\text{AsO}_4$	$\text{Pb}(\text{NO}_3)_2$	3.27

An inspection of this table shows that the only case in which the molecular ratio is very close to 3.00 is in the reaction between lead acetate and excess disodium arsenate. In two cases a product approximating to dilead arsenate was obtained and in all the others basic compounds or mixtures having molecular ratios from 3.14 to 3.36 resulted.

According to Tartar and Robinson the action of aqueous ammonia on dilead arsenate produces, instead of trilead arsenate, a basic arsenate, to which they ascribe the formula  $21\text{Pb}_3(\text{AsO}_4)_2 \cdot 2\text{Pb}(\text{OH})_2 \cdot 10\text{H}_2\text{O}$ . As a result of phase rule experiments (results to be published shortly), we have found that ammonia does change dilead to trilead arsenate, but the latter has a very limited range of existence, and with slight excess of ammonia is converted to a basic arsenate. We have prepared this basic arsenate in crystalline form. All of its properties indicate that it is hydroxy mimetite containing, however, one molecule of water of crystallization,  $\text{Pb}_4(\text{PbOH})(\text{AsO}_4)_3\text{H}_2\text{O}$ . It will be more fully described in a subsequent paper on the basic arsenates of lead.

When small portions of litharge are added to molten lead pyroarsenate combination takes place with incandescence, showing that a chemical reaction, and not merely solution, is taking place. A mixture of dilead arsenate (or pyroarsenate) and litharge in theoretical proportions to form

<sup>1</sup> *Loc. cit.*, p. 203.

<sup>2</sup> *Ibid.*, p. 1847.

trilead arsenate fuses with difficulty before the blast lamp, but can be rendered fluid in a furnace. The melt solidifies to a light yellowish brown, crystalline mass, which is easily broken up. No single crystals were revealed, even after breaking up and examining with the microscope. Most of the pieces were irregularly twinned throughout their mass, giving a speckled appearance when viewed in parallel polarized light. Practically all of the clear transparent pieces appeared to be perpendicular to the acute bisectrix, giving a poor figure very little different from a uni-axial cross. Birefringence low and positive. Specific gravity 7.32 at 15°.

Small portions fused before the mouth blowpipe and allowed to form into hanging drops, on cooling assumed polyhedral forms somewhat resembling crystals of garnet. They were dark brown, iridescent and opaque. The faces were of a resinous luster, somewhat conchoidal in appearance and probably are not true crystallographic faces.

**Lead Metarsenate,  $\text{Pb}(\text{AsO}_3)_2$ .**—Metarsenates in general may be prepared from monoarsenates by ignition. Monolead arsenate loses its water of constitution completely below a red heat and forms lead metarsenate. We also produced it directly from its constituents. When solid arsenic acid and litharge ( $\text{PbO}$ ) or red lead ( $\text{Pb}_3\text{O}_4$ ), in the correct proportion to form lead metarsenate, are heated, the mixture fuses very readily to a rather thin liquid. When permitted to cool slowly, and undisturbed, the melt solidifies at a dull red heat to a transparent glassy mass, very brittle and devoid of crystalline structure. When, however, this material is broken up and the lumps again heated until semiliquid, the whole mass becomes crystalline almost immediately. A product prepared in this way analyzed as follows:

	Found.	Theory for $\text{Pb}(\text{AsO}_3)_2$ .
Lead oxide, $\text{PbO}$ .....	49.75%	49.25%
Arsenic oxide, $\text{As}_2\text{O}_5$ .....	47.12%	50.75%
Arsenious oxide, $\text{As}_2\text{O}_3$ .....	2.65%	.....
	<hr/> 99.52%	<hr/> 100.00%

It is seen that the arsenate has been partially reduced to arsenite, and this occurred even when red lead was used in an attempt to prevent the reduction. A similar experiment, using lead nitrate, produced the same compound. It also contained some arsenite (3.54%  $\text{As}_2\text{O}_3$ ).

**Properties.**—Crystallized lead metarsenate appears to consist of hexagonal tablets. Pieces viewed perpendicular to these tablets were dark under crossed nicols, but gave no recognizable interference figure, even when 1 mm. or more in thickness. All pieces which showed any interference color at all were of an intense blue, regardless of their thickness. This may be the ultra-blue mentioned by Dana<sup>1</sup> as being sometimes seen in minerals such as Danburite, which have very low birefringence.

<sup>1</sup> "Textbook of Mineralogy," p. 428 (1906).

The specific gravity, determined with about 10 g. of material in benzene, was 6.42, referred to water.

Lead metarsenate is decomposed by water. The amorphous glassy material takes up moisture quickly from the air, becoming opaque, but the crystallized product is less readily attacked. Some material powdered to pass a No. 100 sieve was allowed to stand in contact with water at room temperature for 42 hours when it gave only 1.96% soluble  $\text{As}_2\text{O}_5$  and 2.60%  $\text{As}_2\text{O}_3$  (the latter represents the total  $\text{As}_2\text{O}_3$  in the preparation). Boiling for 10 minutes gave practically the same result. However, when ground to an impalpable powder, decomposition into dilead arsenate and arsenic acid occurs almost completely. One gram treated with 100 cc. of water at about  $70^\circ$  for 40 hours gave 21.34%  $\text{As}_2\text{O}_5$  and 2.59%  $\text{As}_2\text{O}_3$  in the solution.

**Lead Pyroarsenates.**—It is theoretically possible to have two lead pyroarsenates, with the formulas  $\text{PbH}_2\text{As}_2\text{O}_7$  and  $\text{Pb}_2\text{As}_2\text{O}_7$ . Pyroarsenic acid and pyroarsenates cannot exist in aqueous solution, and lead pyroarsenates are not obtained by double decomposition. All of our work was therefore confined to ignition methods.

**Monolead Pyroarsenate,  $\text{PbH}_2\text{As}_2\text{O}_7$ .**—This may be regarded as the semidehydration product of monolead orthoarsenate,  $\text{PbH}_4(\text{AsO}_4)_2 = \text{PbH}_2\text{As}_2\text{O}_7 + \text{H}_2\text{O}$ . As a matter of fact, monolead arsenate loses approximately one-half of its water of constitution rapidly at  $150^\circ$  and the remainder is expelled with much more difficulty, as previously noted under monolead arsenate. This is proof that dehydration takes place in steps, and indicates that monolead pyroarsenate is formed as an intermediate product.

Brünnich and F. Smith<sup>1</sup> claim to have found this compound in commercial lead arsenates. Their results, however, are not conclusive and it does not appear, from the properties of this compound, that it could exist in a commercial lead arsenate paste or be isolated from a dry mixture which might contain it by the method employed by these authors.

**Dilead Pyroarsenate,  $\text{Pb}_2\text{As}_2\text{O}_7$ .**—There is a conflict in the literature concerning methods of making this compound. According to Dammer<sup>2</sup> it may be prepared by the action of arsenic acid and air on metallic lead, also by the precipitation of lead nitrate with ammonium, potassium or sodium diarsenates, giving as the reference for the latter statement the work of Berzelius and Mitscherlich. Upon consulting the original articles it was found that Berzelius<sup>3</sup> obtained a product of the percentage composition corresponding to pyroarsenate, but he had ignited the material resulting from the precipitation of lead nitrate by sodium arsenate. Mit-

<sup>1</sup> *Queensland Agric. J.*, 26, 333 (1911).

<sup>2</sup> *Handbuch der Anorganischen Chemie*, 2, Pt. 2, 566 (1894).

<sup>3</sup> *Neues Journal für Chemie und Physik*, 23, 174 (1818).

scherlich<sup>1</sup> quotes Berzelius' results just given and<sup>2</sup> states that "neutral" lead arsenate results by the interaction of lead acetate and "bi-arsenates." The statement by Luther and Volck<sup>3</sup> that lead pyroarsenate results from the action of arsenic acid on basic lead carbonate, and Volck<sup>4</sup> that lead pyroarsenate may occur in lead arsenate pastes, are not supported by experimental proof.

Lefevre,<sup>5</sup> by saturating fused potassium metarsenate with litharge, produced lead pyroarsenate in the form of transparent orthorhombic leaflets.

The simplest means of producing lead pyroarsenate is to heat pure dilead orthoarsenate to about 300°. It may also be made by fusing a mixture of PbO and As<sub>2</sub>O<sub>5</sub>, or Pb(NO<sub>3</sub>)<sub>2</sub> and NH<sub>4</sub>H<sub>2</sub>AsO<sub>4</sub> in equivalent amounts. Fusion always results in a slight reduction to arsenite.

*Properties.*—Lead pyroarsenate melts before a blast lamp, becoming quite fluid, and solidifies on cooling to a light yellow crystalline mass, which is easily broken and powdered between the fingers, probably owing to pronounced cleavage in the crystals. The crushed material when examined under the polarizing microscope showed no well formed crystals but a predominance of irregular pieces almost perpendicular to one optic axis. Such pieces, whenever they had any straight edges, showed slightly inclined extinction. They were biaxial and positive, with medium birefringence.

The specific gravity, determined on about 55 g. of material in benzene, was found to be 6.85 referred to water.

Lefevre states<sup>6</sup> that lead pyroarsenate crystals slowly became opaque under the action of water. We found that when finely powdered it rapidly absorbs water when moistened. Amorphous dilead arsenate, heated to redness but not fused, lost 2.73%. When moistened and allowed to stand for three days and then dried at 110°, it regained 2.29%. A second moistening and drying resulted in a further gain of 0.29% or a total of 2.58%, which is the theoretical amount of water of constitution in dilead arsenate.

### Summary.

1. Monolead arsenate has been prepared and its physical and chemical properties described for the first time.
2. The methods of preparing crystalline dilead arsenate have been reviewed, and its physical and chemical properties more fully investigated.
3. Crystallized trilead arsenate has been prepared.

<sup>1</sup> *Ann. chim. phys.*, [2] 19, 360 (1821).

<sup>2</sup> *Ibid.*, p. 368.

<sup>3</sup> U. S. Patent No. 903,389.

<sup>4</sup> *Science*, 33, 868 (1911).

<sup>5</sup> *Ann. chim. phys.*, [6] 27, 25 (1892).

<sup>6</sup> *Loc. cit.*

4. Lead metarsenate has been made and its physical and chemical properties described.

5. Dilead pyroarsenate has been prepared in crystalline form, and certain of its physical and chemical properties determined.

INSECTICIDE AND FUNGICIDE LABORATORY,  
MISCELLANEOUS DIVISION, BUREAU OF CHEMISTRY,  
WASHINGTON, D. C.

[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR., CHEMICAL LABORATORY OF HARVARD COLLEGE.]

## THE EFFICIENCY OF CALCIUM CHLORIDE, SODIUM HYDROXIDE AND POTASSIUM HYDROXIDE AS DRYING AGENTS.

BY GREGORY P. BAXTER AND HOWARD W. STARKWEATHER.

Received August 19, 1916.

In a recent paper upon the efficiency of certain drying agents, Baxter and Warren<sup>1</sup> make the statement that Dibbitts<sup>2</sup> found the aqueous vapor pressures of the lowest hydrate of calcium chloride to be 0.29 mm., 2.17 mm., and 3.50 mm. at 0°, 24° and 30°, respectively. Our attention has been called by Dr. W. F. Hillebrand to the fact that these figures refer to a hydrate containing 26% of water. As we have been unable to discover reliable data upon the drying efficiency of anhydrous calcium chloride,<sup>3</sup> the matter has been investigated experimentally. We have found the efficiency of this salt to be far greater than the above values indicate. In addition we seized the opportunity to test two other common drying agents, fused sodium and potassium hydroxides.

The air current method was employed, the details of the apparatus and procedure being essentially identical with those described by Baxter and Warren. Calcium chloride was prepared in an anhydrous condition by fusion in an open platinum dish.<sup>4</sup> While still warm it was crushed to pieces the size of a small pea and packed in a glass stoppered U-tube about 15 mm. in diameter, the column of salt being about 30 cm. long.<sup>5</sup> In most of the experiments the air was passed over a 20% solution of sodium hydroxide to ensure an excess of moisture before being conducted through the calcium chloride tube. After a considerable amount of moisture had been absorbed by the calcium chloride, in a few experiments the air was first dried by means of concentrated sulfuric acid in order that the equilibrium might be approached from the reverse side. The

<sup>1</sup> THIS JOURNAL, 33, 340 (1911).

<sup>2</sup> *Z. anal. Chem.*, 15, 159 (1876).

<sup>3</sup> See however, Marden and Elliott, *J. Ind. Eng. Chem.*, 7, 320 (1915).

<sup>4</sup> The calcium chloride was undoubtedly basic after fusion. It is, however, unlikely that the basic impurity was present in quantity sufficient to affect the results even if of a greater efficiency than the neutral salt.

<sup>5</sup> In the paper by Baxter and Warren it is erroneously stated that the column of salt was 30 mm. long, as in reality it was ten times this length.

results with calcium chloride at  $0^{\circ}$  and  $25^{\circ}$  were very consistent and satisfactory, but the first experiments at  $50^{\circ}$  showed gradually higher values for succeeding experiments. Fearing that the chloride had by this time absorbed so much water that its efficiency had been impaired, the salt was again fused. While the results then became more nearly concordant, irregularities still persisted, until the layer of active salt was doubled to about 70 cm. by inserting a second U-tube containing the fused salt. The results then showed the most satisfactory agreement. In order to find out whether the layer of chloride had been sufficiently long at the lower temperatures, additional experiments, Nos. 4, 5, 13, 14, were carried out at the lower temperatures with the longer layer, with results identical with the earlier ones.

TABLE I.— $\text{CaCl}_2$  AS DRYING AGENT.

Number of experiment.	Temperature.	Condi- tions of experiment.	Liters per hour.	Liters of air. (0°; 760 mm.)	Mg of water.	Cc. of water vapor. (0°; 760 mm.)	Internal pressure of system. Mm.	Pressure of water vapor. Mm.
1	0°	Moist	1.1	5.8	0.41	0.51	770	0.07
2		Moist	1.0	5.8	0.45	0.56	763	0.07
3		Moist	1.2	5.8	0.50	0.62	764	0.08
4		Moist	2.3	5.7	0.50	0.62	750	0.08
5		Dry	1.5	5.8	0.40	0.50	761	0.07
Average,								0.07
6	25°	Moist	1.3	6.38	1.85	2.30	758	0.27
7		Moist	0.8	5.71	1.93	2.40	761	0.32
8		Moist	0.8	5.82	2.43	3.02	768	0.40
9		Moist	1.0	5.73	2.15	2.67	761	0.35
10		Moist	1.2	5.84	1.97	2.45	770	0.32
11		Moist	2.3	5.78	2.00	2.49	768	0.33
12		Moist	1.0	5.66	2.40	2.99	752	0.39
13		Moist	1.0	5.63	1.90	2.36	746	0.31
14		Dry	2.0	5.67	2.01	2.50	750	0.33
Average,								0.34
15	50°	Dry	1.2	5.72	8.18	10.17	758	1.35
16		Moist	2.3	5.66	7.96	9.90	752	1.32
17		Dry	1.3	5.76	7.80	9.70	765	1.28
18		Moist	1.3	5.63	8.17	10.16	749	1.35
19		Dry	2.9	5.69	8.60	10.70	751	1.41
20		Moist	0.9	5.59	8.08	10.05	738	1.33
Average,								1.34

The attempt was made to weigh the phosphorus pentoxide tube in which the water was absorbed to hundredths of a milligram, by using a No. 10 Troemner balance and gold plated weights carefully standardized by the Richards method. No claim is made, however, that the accuracy

is greater than a tenth of a milligram. It was repeatedly shown that the tube remained constant in weight within this amount for periods of fourteen to sixteen hours.

No blank experiments were considered necessary, since in the runs with potassium hydroxide the gain in weight of the tube was scarcely perceptible.

While three points are obviously insufficient to define a curve exactly, since the plot of the logarithm of the vapor pressure against the reciprocal of the absolute temperature is very nearly a straight line it seems worth while to point out that the preceding averages can be represented by the modification of the Antoine<sup>1</sup> formula

$$\log v. p. = 8.614 - \frac{3234}{T + 58}$$

The desiccating efficiency of sodium hydroxide was determined in the same manner as that of calcium chloride, using the two tubes (70 cm.) of drying agent. The sodium hydroxide was fused in a silver dish and broken up while still warm. Apparently the greater part of the water was absorbed by the first 5 cm. of the hydroxide.

TABLE II.—NaOH AS DRYING AGENT.

Number of experiment.	Temperature.	Con- ditions of experiment.	Liters per hour.	Liters of air. (0°; 760 mm.)	Mg. of water.	Cc. of water vapor. (0°; 760 mm.)	Internal pressure of system. Mm.	Pressure of water vapor. Mm.
1	0°	Moist	2.0	11.6	0.60	0.75	765	0.05
2		Dry	2.0	11.4	0.35	0.44	755	0.03
3		Moist	1.6	11.3	0.40	0.50	745	0.03
Average, 0.04								
4	25°	Moist	2.0	11.43	2.00	2.49	756	0.16
5		Moist	1.1	5.69	0.90	1.12	752	0.15
6		Dry	2.0	11.43	1.82	2.26	756	0.15
Average, 0.15								
7	50°	Moist	1.4	5.69	6.82	8.48	756	1.13
8		Dry	1.7	11.42	14.07	17.50	761	1.16
9		Moist	1.7	11.55	13.90	17.30	763	1.15
Average, 1.15								

The experimental values may be computed from the expression

$$\log v. p. = -4.041 - \frac{373.3}{(T - 414)}$$

Potassium hydroxide was next investigated in the same way. The potassium hydroxide was fused in a silver dish and while still warm was broken into small pieces and transferred to the drying tubes. Two experiments at 25°, and two more at 50°, each involving nearly twelve

<sup>1</sup> *Compt. rend.*, 110, 632 (1890); 112, 284 (1891); 113, 328 (1892); 116, 170 (1893).



liters of air, gave changes in the weight of the phosphorus pentoxide tube no greater than the error of weighing. Then two experiments at 50°, each extending over three days, were performed. Air was actually passing through the apparatus only during the day; at night all stop-cocks were closed.

TABLE III.—KOH AS DRYING AGENT.

Number of experiment.	Temperature.	Conditions of experiment.	Liters per hour.	Liters of air. (0°; 760 mm.)	Mg. of water.	Cc. of water vapor. (0°; 760 mm.)	Internal pressure of system. Mm.	Pressure of water vapor. Mm.
1	50°	Moist	2.0	39.9	0.28	0.35	759	0.007
2		Moist	2.3	45.6	0.34	0.42	759	0.007

Average, 0.007

As pointed out by Morley<sup>1</sup> there is a possibility, in these long experiments, that water diffused through the rubber connections, or was formed by oxidation of the rubber.<sup>2</sup> In view of this possibility the results are to be considered as maxima. No weighable amount of moisture could have passed the pentoxide, since Morley<sup>3</sup> found that phosphorus pentoxide leaves not more than one milligram of water in 40,000 liters of air.

The noteworthy facts shown by the foregoing results are (1) the very considerable temperature coefficients in the case of calcium chloride and sodium hydroxide,<sup>4</sup> and (2) the remarkable efficiency of potassium hydroxide even at 50°. Judging from the temperature coefficients of the other two salts, potassium hydroxide at 25° is fully as efficient as sulfuric acid.

To summarize the results of this research, the aqueous vapor pressures of the lowest hydrates of the salts examined have the following maximum values:

	0°. Mm.	25°. Mm.	50°. Mm.
CaCl <sub>2</sub> .....	0.07	0.34	1.34
NaOH.....	0.04	0.15	1.15
KOH.....	..	..	0.007

The weights of residual water in one liter of a gas dried at 25° by these compounds, calcium bromide, zinc chloride, zinc bromide and sulfuric acid are:

Substance.....	CaCl <sub>2</sub>	CaBr <sub>2</sub>	ZnBr <sub>2</sub>	ZnCl <sub>2</sub>	NaOH	KOH (50°)	KOH <sup>5</sup>	H <sub>2</sub> SO <sub>4</sub>
Milligrams.....	0.36	0.2	1.1	0.8	0.16	0.007	0.002	0.003

CAMBRIDGE, MASS.

<sup>1</sup> *Am. J. Sci.*, 30, 441 (1885).

<sup>2</sup> Only one very short rubber connection was used in our apparatus before the air reached the phosphorus pentoxide tube.

<sup>3</sup> *Am. J. Sci.*, 34, 199 (1887); *THIS JOURNAL*, 26, 1171 (1904).

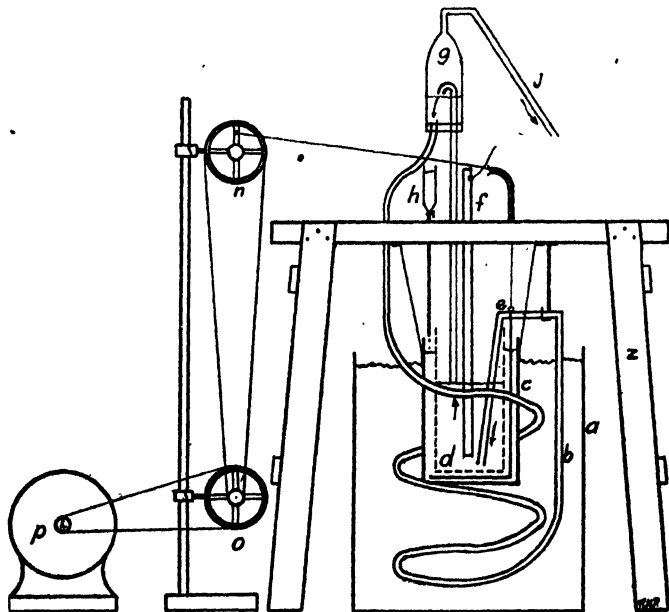
<sup>4</sup> Baxter and Warren found similar increments with rising temperature with the salts examined.

<sup>5</sup> Estimated from the temperature coefficient of the other salts.

## NOTES.

**The Electrolytic Preparation of Hydroxylamine Hydrochloride.**—The extensive use of hydroxylamine hydrochloride in the electroanalytical determination of metals according to the methods devised in this laboratory (see Schoch and Brown, *THIS JOURNAL*, **38**, 1660 (1916)), and the utter absence of this substance in the market at present rendered it necessary for us to prepare hydroxylamine hydrochloride in lots of several hundred grams. After trying various other methods, we found its preparation by electrolytic reduction from nitric acid according to the method of Julius Tafel<sup>1</sup> to be very convenient. Since, under the present circumstances, others may desire to make this material, we thought they might wish to learn how the method works, and to benefit by the changes in procedure which we have made.

The apparatus shown in the accompanying sketch is identical with that used by Tafel except that the anode (*f*) is a lead rod or pipe, about one inch in diameter; this was used in place of the graphite anode employed by Tafel because we found it necessary to use dilute sulfuric acid in the



Apparatus for electrolytic preparation of  $\text{NH}_2\text{OH}$ ,  $\text{HCl}$ .

anode compartment. The lead cup or cathode (*c*) has a diameter of 10 cm. and a height of 18 cm. Its inner surface was well amalgamated. When used continuously, it had to be re-amalgamated once a week. The porous cup (*d*) has an internal diameter of 6.5 cm. and a height of 19 cm.

<sup>1</sup> *Z. anorg. Chem.*, **31**, 289.

The space between these (the cathode compartment) holds about 400 cc., and is filled with a mixture of three volumes of water to one volume of hydrochloric acid (sp. gr. 1.20). Although the cathode liquid is kept cool by surrounding the lead cup with a freezing mixture (in the pail *a*), yet the anode liquid has to be cooled also; this is accomplished by connecting (*j*) to a suction pump and drawing the anode liquid through the glass tube (*s*) into the glass "adapter" (*g*). The latter is closed at the bottom by a two-holed rubber stopper; a  $1\frac{1}{2}$  in. lead pipe ( $\frac{1}{4}$  in. bore), 10 ft. long, has one end thrust through one of these holes at the bottom of (*g*) and is bent into a coil placed in the freezing mixture as shown. The anode liquid flows, by gravity, from (*g*) through the lead pipe, and then, through a glass tube extension to the bottom of the porous cup. A glass stirrer serves to stir the cathode liquid; its upper end is shown at (*e*). Its lower end is bent into circular form so as to fit between the lead cup and the porous cup. The stirrer is raised and lowered by the mechanical arrangement shown. The nitric acid is dropped in through the dropping funnel (*h*).

To operate the apparatus, the anode compartment is filled with dilute sulfuric acid, the cathode compartment with hydrochloric acid of the required concentration, and the pail with a freezing mixture. When the liquids in the cell has attained a temperature of  $15^{\circ}$  or less, a current of 50 amperes is turned on (pressure, 25 volts!), and then a mixture of nitric acid (sp. gr. 1.40) with one volume of water is allowed to drop into the cathode compartment through (*h*) at such a rate that  $2\frac{1}{2}$  hrs. are required to add 75 cc. of the nitric acid mixture. After this amount of nitric acid had been added, the current is allowed to continue to flow for 30 minutes longer, or a total of three hours. The current density in the above procedure is 8 amps. per 100 sq. cm.

After the end of three hours of electrolysis, the cathode liquid is removed by syphoning, and concentrated *in vacuo*, by heating it on top of a water bath; the flask should not be touched by the water in the water bath. The common practice of drawing air through the distilling flask must naturally not be employed. When the liquid has been concentrated to such an extent that crystals are formed in the drops spattered on the sides of the flask, it is removed and cooled in a freezing mixture without stirring (to avoid possible decomposition of the hydroxylamine by the oxygen of the air). The crystals are gathered on a filter paper, and the mother liquor is concentrated further to secure a second crop of crystals, and again a third crop; with the third crop the liquid may be evaporated almost completely.

To free the hydroxylamine hydrochloride from the accompanying ammonium chloride, the crude material is treated with separate small portions of cold absolute alcohol until a test shows that the residue is free

from hydroxylamine hydrochloride. In explanation of this procedure, it should be mentioned that one liter of alcohol at 15° dissolves 44.3 grams of hydroxylamine hydrochloride, and only 6.2 grams of ammonium chloride.

The hydroxylamine hydrochloride is obtained from the alcoholic solution by the same procedure as that employed for its crystallization from the cathode liquid above. In one case—which is typical—we obtained 45.7 grams of this “purified” material from 37.5 cc. of nitric acid (sp. gr. 1.40). If we deduct from this the maximum weight of ammonium chloride possibly mixed with it, we find that the yield of pure hydroxylamine hydrochloride is about 80% of the theoretical amount possible.

This work was done by Mr. R. H. Pritchett of this laboratory.

E. P. SCHOCH AND R. H. PRITCHETT.

UNIVERSITY OF TEXAS,  
AUSTIN, TEXAS.

**Inclusions in the Silver Voltameter.**—In a very interesting and important paper on the inclusions of mother liquor in the crystals deposited in the silver coulometer<sup>1</sup>, Vinal and Bovard have determined the weight of mother liquor thus held, under the most satisfactory conditions which have been worked out with much care by the Bureau of Standards. They find it to be on the average 0.004 %—an amount only about one-quarter of our average value, but identical with the lowest which we found under our conditions. This is a contribution of great importance, for it gives positive information on the only important point previously in doubt about this work of the Bureau as regards the electrochemical equivalent of silver. It seems, indeed, by thus completing the investigation, to place this work of the Bureau, carried out under Professor E. B. Rosa, on a higher plane than any other which has ever been published concerning this important constant.

The small amount of inclusion thus found by the Bureau of Standards justifies the great care taken there to maintain adequate purity of the electrolyte. In this connection we wish to point out again<sup>2</sup> that these investigators were the first to investigate the precise effects of organic impurities on the weight of the deposit. A previous statement of ours<sup>3</sup> was not intended to claim priority of any such detailed knowledge; it was intended only to express the fact that the desirability of purity of electrolyte had been recognized in early work on general grounds. In all of the 56 “standard” electrolytes made at Harvard in 1901<sup>4</sup> with the porous cap coulometer, organic matter of all kinds was scrupulously ex-

<sup>1</sup> *Bull. Bur. Standards*, Reprint 271 (1916); *THIS JOURNAL*, 38, 496 (1916).

<sup>2</sup> Richards and Anderegg, *THIS JOURNAL*, 37, 692 (1915).

<sup>3</sup> *Ibid.*, 37, 8 (1915).

<sup>4</sup> Richards and Heimrod, *Proc. Am. Acad.*, 37, 415 (1902).

cluded from the electrolyte, both in preparation and during the electrolysis; but no effort was made to discover the part played by filter paper in affecting the weight of the deposit (recognized as too great) in the filter-paper coulometer. The excess of weight was then ascribed primarily to another cause, namely, the possible existence of a complex ion formed at the anode. The investigators at the Bureau of Standards have shown that the effect of filter paper is considerable, and believe indeed that its presence is the only cause of the excess.

Another important feature of the interesting paper of Vinal and Bovard was the discovery of a hitherto unsuspected source of error in the silver coulometer—namely, the effect of platinum black (remaining from a previous determination) upon the weight of silver deposited and upon the inclusion. Although recognizing the presence of traces of platinum black after the gently ignited silver had been dissolved, we did not suspect that this substance could affect a subsequent trial, because we thought that we were able to remove it wholly by scrubbing. But Vinal and Bovard have shown that even minute traces of platinum black, imperceptible to the eye, may have an appreciable effect upon the new deposit. Our oversight was in omitting to ignite the cathode at a high temperature between each trial<sup>1</sup>—a precaution which we can now see to be essential. On account of this error in experimentation, it is clear that our more subtle conclusions, especially that concerning the “volume effect” and the comparison of the Kohlrausch coulometer with the porous cup form, may have been invalidated. The amount of residual platinum black in our cathodes cannot be decided without further trial (now in progress) under precisely similar conditions; it must have been very small. The uncertainty introduced into our results is perhaps less than one part in ten thousand in the weight of the ignited silver;<sup>2</sup> but, nevertheless, small as the effect is in relation to the weight of silver, it is important in relation to the small divergencies upon which some of our conclusions were based.

Other less important minor points in connection with the irregularities of the coulometer are receiving further experimental attention, here and elsewhere. Discussion of all these points had better await the results. So far as we can see, none of the still unsettled questions affects appreciably the main outcome of the work of the Bureau of Standards, as regards the magnitude of the electrochemical equivalent of silver. This is now established by this recent paper of Vinal and Bovard, in an unusually impregnable position.

In brief, this note is intended to express our satisfaction that the ad-

<sup>1</sup> In our experiments the crucible was merely heated at 160° until constant in weight between each trial.

<sup>2</sup> This conclusion is based upon preliminary experiments carried out here by N. F. Hall.

mirable work of the Bureau of Standards has been completed by the determination of the actual amount of inclusion in their deposits; to emphasize the fact that in view of the newly discovered effect of invisible traces of platinum black, we overrated the significance and certainty of some of our recent conclusions, reasonable although they seemed at the time; and to state that further experiments are in progress.

T. W. RICHARDS AND F. O. ANDEREGG.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

## MOLECULAR REARRANGEMENTS OF $\beta$ -TRIPHENYLMETHYL- $\beta$ -METHYL HYDROXYLAMINES AND THE THEORY OF MOLECULAR REARRANGEMENTS.<sup>1</sup>

BY JULIUS STIEGLITZ AND BERT ALLEN STAGNER.<sup>2</sup>

Received August 1, 1916.

The earliest observations of molecular rearrangements of hydroxylamine derivatives were those of Lossen<sup>3</sup> in the case of hydroxamic acids,  $\text{RCO} \cdot \text{NHOH}$ , and of dihydroxamic acids,  $\text{RCO} \cdot \text{NHOCOR}_1$ .<sup>4</sup> In explanation of these and similar rearrangements, the one of us proposed the theory<sup>5</sup> that they take place through the intermediate formation of univalent nitrogen derivatives under the influence of the reagent used to effect the rearrangement. Thus, a hydroxamic acid could form such a univalent nitrogen derivative by the loss of water in the presence of dehydrating agents.



Dihydroxamic acids would yield the same products with the loss of a molecule of acid under the influence of bases or heat.



The free or latent valences of the unsaturated nitrogen atom were considered to have the power to take the radical R from the carbon atom. Of the many facts brought out in support of this theory by the one of us and by a number of independent investigators,<sup>6</sup> only the most important need be summarized here: (1) The ready application of the theory

<sup>1</sup> A brief preliminary report appeared in *Proc. Nat. Acad. Sciences*, **1**, 205 (1915). For literature references to previous papers, see Stieglitz and Leech, *THIS JOURNAL*, **36**, 272 (1914).

<sup>2</sup> The material presented here is used by Stagner in his dissertation in part fulfillment of the requirements for the Ph.D. degree of the University of Chicago.

<sup>3</sup> *Ann.*, **161**, 359 (1872).

<sup>4</sup> This is tautomeric with  $\text{RC}(\text{OH}) : \text{NO} \cdot \text{COR}_1$ .

<sup>5</sup> See the literature references given by Stieglitz and Leech, *loc. cit.*

<sup>6</sup> Schroeter, *Ber.*, **42**, 2340 (1909); **44**, 1207 (1911); Stoermer, *Ibid.*, **42**, 3133; Wieland, *Ibid.*, **42**, 4207; L. W. Jones, *Am. Chem. J.*, **48**, 1 (1912); **50**, 440 (1913).

without any further assumptions, to Hofmann's rearrangement of acyl halogenamides, to the Curtius rearrangement of acyl azides, to the rearrangement of triphenylmethyl hydroxylamines, halogen amines and azides, as investigated by the one of us and his collaborators. (2) The *non-occurrence* of rearrangements of compounds  $\text{RCO.N}(\text{CH}_3)\text{OH}$ ,<sup>1</sup>  $\text{RCO.N}(\text{CH}_3)\text{Cl}$ ,  $\text{RC}(:\text{NCl})\text{OCH}_3$ ,<sup>2</sup> which appear to have everything in common with the rearranging substances except the possibility of readily forming univalent nitrogen derivatives. (3) The close relation the reagents used to effect each rearrangement bear to the facilitating of a dissociation leading to univalent nitrogen derivatives (see Equations 1 and 2).

No other theory of the rearrangements, that has been proposed, could give as complete an explanation of any one of these sets of facts, we believe, not to speak of all three of them.

In recent years the initial force leading to the rearrangements has been more sharply defined, on the basis of the electron theory of valence, as *residing in the instability of the charges on the radicals held by the nitrogen* in the various classes of rearranging compounds and to the great tendency of these radicals to go over into their common stable forms.<sup>3</sup> This tendency has been compared with the electrolytic solution tension of elements.<sup>4</sup> Thus, in the hydroxylamine derivatives  $\text{RCO.NH}^+ + \text{OH}^-$ ,<sup>5</sup> we have to deal with the tendency of the positive OH radical to go over into its common negative form; in the chloroamines,  $\text{RCO.NH}^+ + \text{Cl}^-$ ,<sup>6</sup> we have positive chlorine with its enormous tendency to form its stable negative atom or ion. In satisfying these tendencies by the absorption of electrons from neighboring atoms, these radicals ( $^+\text{OH}$ ,  $^+\text{Cl}$ ,  $^+\text{Br}$ , and also<sup>7</sup>  $^+\text{N}$ , etc.) disturb the valence electrons of the neighboring atoms in the compounds under discussion and rearrangement is inevitable. Whatever view of the mechanism of the rearrangements may finally obtain, this, it

<sup>1</sup> This question is being re-investigated by Miss Quaesita Drake, as a result of the work described in this paper.

<sup>2</sup> Destruction distillation effects a rearrangement and the loss of methylchloride (Stieglitz, Earle and W. J. Hale, unpublished work).

<sup>3</sup> The electron interpretation of the rearrangements was presented independently and practically simultaneously (see *THIS JOURNAL*, 36, 287 (1914)) by L. W. Jones (*Am. Chem. J.*, 50, 448, published at the end of January, 1914) and by one of us (February number of *THIS JOURNAL* (1914)). The interpretations differ in some important respects, but they agree as to the fundamental relations. Preliminary suggestions were made by Stieglitz, *Ber.*, 43, 782 (1910); *Am. Chem. J.*, 46, 327 (1911); *Ber.*, 46, 2149 (1913), and by Jones, *Am. Chem. J.*, 48, 1 (1912). The same idea, expressed in the older terms then current, was clearly recognized in the earlier papers on the rearrangement of acyl halogen amides (Hoogawerff and van Dorp, *Rec. trav. chim.*, 8, 173 (1889); Lengfeld and Stieglitz, *Am. Chem. J.*, 15, 215, 504 (1893)).

<sup>4</sup> Stieglitz, *THIS JOURNAL*, 36, 276, 280 (1914).

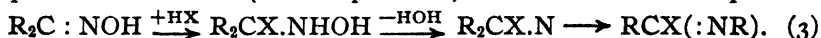
<sup>5</sup> *Ibid.*

<sup>6</sup> *Ibid.*, and *Ber.*, 43, 782 (1910); 46, 2149 (1913).

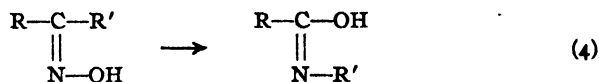
<sup>7</sup> In hydrazine derivatives, including probably the azides, we have the unstable radical  $^+\text{N}^-$  (Stieglitz and Curme, *Ber.*, 46, 911 (1913)).

seems to us, is the most vital consideration<sup>1</sup> and should form the common ground on which all theories of the rearrangements must meet.

The one arrangement for which, from the outset, any further special assumptions had to be made in the univalent nitrogen theory has been the Beckmann rearrangement of oximes. For this rearrangement, under the influence of acid dehydrating agents, the one of us assumed, provisionally,<sup>2</sup> that the rearrangement is preceded by the absorption of acid and the subsequent loss of water (or its equivalent) as indicated in the equation



This interpretation seemed to be borne out by the proof that triaryl-methylhydroxylamines,  $R_3C.NHOH$ , of exactly the same structure as the assumed intermediate product,  $R_2CX.NHOH$ , rearrange in exactly the same way and under the same conditions.<sup>3</sup> But the assumption met difficulties<sup>4</sup> in explaining the observed differences in the migration of the radicals  $R$  and  $R'$  of stereoisomeric oximes  $RR'C : NOH$ . In this one case the conception of a direct exchange of radicals, *e. g.*:



as postulated by Beckmann,<sup>5</sup> seemed to agree with the facts rather better than the univalent nitrogen theory. In view of this fact, attempts have been included in all the investigations planned by the one of us, to effect this type of rearrangement with compounds which could not be expected to form a univalent nitrogen derivative without an easily recognized destructive change in the product. Compounds of the type  $RCO.N(Alkyl)-OH$ ,  $RCO.N(Alkyl)Cl$ , had been used for this purpose. All efforts to rearrange such compounds had given negative results, but the attempts were repeated with every new class of compounds investigated. A first clue to such a rearrangement was finally discovered last year, when the one of us, together with Leech,<sup>6</sup> examined the effect of phosphorus pentachloride on  $\beta$ -triphenylmethyl- $\beta$ -methylhydroxylamine,  $(C_6H_5)_3C.NCH_3.OH$ . The product of the action seemed to give methylaniline on hydrolysis and this could only be formed as the result of a rearrangement.

<sup>1</sup> See also L. W. Jones, *loc. cit.*

<sup>2</sup> *Am. Chem. J.*, 18, 754 (1896) (footnote), and *THIS JOURNAL*, 36, 277 (1914), footnote 2.

<sup>3</sup> Stieglitz and Leech, *Ber.*, 46, 2147 (1913).

<sup>4</sup> Stieglitz, *Am. Chem. J.*, 18, 754 (1896); Montague, *Ber.*, 43, 2014 (1910); L. W. Jones, *Am. Chem. J.*, 48, 28 (1912).

<sup>5</sup> *Ber.*, 19, 988 (1886); 27, 300 (1894). Other prominent adherents of this view, in one form or another, have been Hoogewerff and van Dorp, *Rec. trav. chim.*, 8, 173 (1889); Hantzsch, *Ber.*, 24, 3516 (1891); Kuhara, *Mem. Coll. Sci. Eng. Kyoto*, 1, 254 (1903-1908); 2, 367 (1909-1910); 6, 1 (1913); *Mem. Coll. Sci. Kyoto*, 1, 25 (1914).

<sup>6</sup> *THIS JOURNAL*, *loc. cit.*



The yield of methylaniline was so small, however, that the evidence of its formation was limited to the characteristic chloride of lime color test, discovered by Leech,<sup>1</sup> and of the melting-point tests of the acetyl derivative. It was not beyond the range of possibility that the substance resulted from an alkylation of aniline rather than as a primary product of rearrangement. Under the circumstances, an exhaustive investigation of the reaction was undertaken by us. The results of this work and the conclusions drawn from it are presented in this paper.

It should be said at once that the observations of Stieglitz and Leech have been confirmed in every respect and conclusive evidence brought that methylaniline is formed in quantity by the hydrolysis of the product of the rearrangement of  $\beta$ -triphenylmethyl- $\beta$ -methylhydroxylamine.<sup>2</sup> The methylaniline was identified by the analysis of its chloroplatinate, by the examination of its hydrochloride, as well as, again, by its characteristic reaction with chloride of lime. It was not considered necessary to repeat the identification as acetylmethylaniline.

Furthermore, *benzophenone* has been isolated and identified by us as the compound formed, with methylaniline, in the hydrolysis of the product of rearrangement.

The demonstrated rearrangement of  $\beta$ -triphenylmethyl- $\beta$ -methylhydroxylamine must be considered to open up the whole problem of the theory of the molecular rearrangements outlined above: *the formation of a simple univalent nitrogen derivative,  $R_3C.N$ , is impossible* in this case. Of the various theories which suggested themselves<sup>3</sup> when the first indication of this rearrangement was obtained, an important one is excluded by the identification of benzophenone just mentioned: the possibility of a primary dissociation of triphenylmethymethylhydroxylamine into a *bivalent* nitrogen derivative,<sup>4</sup> corresponding to the dissociation of the related triphenylmethylperoxide into a univalent oxygen derivative, with a subsequent rearrangement, as discovered by Wieland,<sup>5</sup> is excluded<sup>6</sup> by the formation of benzophenone. A rearrangement proceeding along these lines should yield tetraphenylbenz pinacone by hydrolysis of the product.<sup>7</sup> Not the slightest indication of the presence of the pinacone was observed, although a careful search for it was made. The pinacone is known to be decomposed by heat into benzophenone and benzhydrol,

<sup>1</sup> THIS JOURNAL, 35, 1042 (1913).

<sup>2</sup> The behavior of acyl- $\beta$ -hydroxylamines,  $RCON(CH_3)OH$  and similar compounds is being re-investigated by Miss Quaesita Drake as a result of this work.

<sup>3</sup> Stieglitz and Leech, *loc. cit.*, p. 284.

<sup>4</sup> *Loc. cit.*, p. 286.

<sup>5</sup> *Ber.*, 44, 2550 (1911).

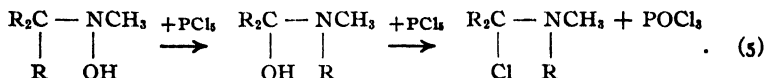
<sup>6</sup> A modification of this theory is discussed further on.

<sup>7</sup> This is readily apparent from a consideration of the product given in Equation

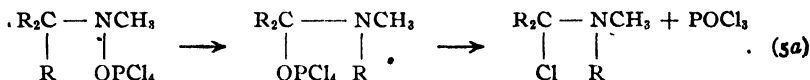
17, THIS JOURNAL, 36, 286 (1914).

but no such decomposition takes place under the conditions obtaining in the reaction studied by us: this was confirmed by parallel experiments carried out with a preparation of the pinacone.

This leaves only two important theories that we need take into account:<sup>1</sup> first, the theory of Beckmann that the rearrangements involve simply direct exchanges of radicals (see Equation 4), the reagents used acting "catalytically." For the rearrangement of  $\beta$ -triphenyl- $\beta$ -methylhydroxylamine we would have



A variation of this view, which finds its chief modern support in the important work of Kuhara,<sup>2</sup> is that in the rearrangement of hydroxylamine derivatives under the influence of acetyl chloride, acetic anhydride, sulfuric acid, etc., it is not the OH radical that migrates but an acyl derivative of it,  $\text{RCO.O-}$ . This view is practically identical with Beckmann's first interpretation<sup>3</sup> of the reaction that bears his name. From this point of view, as understood now, phosphorus pentachloride presumably reacts first on a hydroxylamine derivative like triphenylmethyl-methylhydroxylamine to form the product  $\text{R}_3\text{C.N}(\text{CH}_3)\text{OPCl}_4$ ,<sup>4</sup> which then rearranges according to



In the second place, we have the theory of the intermediate formation of univalent (or other unsaturated) nitrogen derivatives in these and re-

<sup>1</sup> All other theories that have been proposed are quite untenable in view of the facts now known; the formation of ring derivatives in which the nitrogen is connected with the migrating alkyl or aryl radical (Nef, *Ann.*, **298**, 308 (1897); **318**, 39, 227 (1901)), is incompatible with the position the nitrogen invariably takes in the migrating alkyl or aryl (cf. Stieglitz, *Am. Chem. J.*, **29**, 58 (1903)). The formation of

unstable triatomic rings,  $\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{C} \quad | \\ \quad \text{NH} \end{array}$ , proposed by v. Baeyer as a result of his observa-

tions of rearrangements of peroxides  $\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{C} \quad | \\ \text{O} \quad \text{O} \end{array}$  (*Ber.*, **32**, 3627 (1900)) is quite impossible

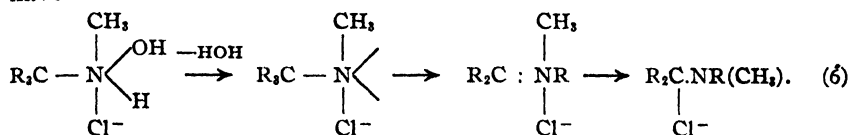
in view of the fact that triphenylmethyl derivatives, such as  $(\text{C}_6\text{H}_5)_3\text{C.NHCl}$  behave exactly as do the acyl derivatives; they cannot possibly form the rings demanded by Baeyer's theory. (See below, p. 2060, and see also, Stieglitz, *Am. Chem. J.*, **29**, 49 (1903), and Wieland, *Ber.*, **42**, 4207 (1909)).

<sup>2</sup> *Loc. cit.* See also Sluiter, *Rec. trav. chim.*, **24**, 372 (1905).

<sup>3</sup> *Ber.*, **19**, 988 (1886).

<sup>4</sup> Werner, *Ber.*, **25**, 40 (1892); Stieglitz and Leech, *THIS JOURNAL*, **36**, 279 (1914). The assumption of this intermediate product would be in far better agreement with the facts than the assumption of the intermediate formation of N-Cl derivatives, as made by Beckmann and others.

lated rearrangements. The observation that phosphorus pentoxide effects the rearrangement of triphenylmethyl hydroxylamine *hydrochloride*<sup>1</sup> suggested to the one of us the possibility that *salts* of hydroxylamines, by being deprived of water or its equivalent, could form *salts* of univalent nitrogen compounds, which could rearrange in exactly the same way as the univalent nitrogen compounds R<sub>3</sub>C.N. We would have<sup>2</sup>



These two theories,<sup>3</sup> it seems to us, are worthy of critical consideration on the basis of the new facts discovered,<sup>4</sup> and we shall indicate here, as briefly as possible, the facts, as at present known, which appear to favor the one theory or the other. We shall then attempt to show the common ground, on which both theories rest.

I. The following facts at present seem to us to weigh in favor of Beckmann's theory of a direct exchange of radicals (see Equations 4, 5 and 5a): 1. We have the fact, now established by us, that triphenylmethyl-β-methylhydroxylamine is rearranged in the same way and under the same conditions as triphenylmethylhydroxylamine itself. For the rearrangement to proceed by way of the hydrochloride of a univalent nitrogen derivative (Equation 6), it would be necessary to assume the temporary

existence of a compound, which we will call Compound A,  $\text{R}_3\text{C}^+ \begin{array}{c} +\text{CH}_3 \\ | \\ \text{N} \begin{array}{l} \nearrow \\ \searrow \end{array} \\ + \\ | \\ -\text{Cl} \end{array}$

and which would be an *electromer* of a compound B, triphenylmethyl-

chloromethylamine,  $\text{R}_3\text{C}^+ \begin{array}{c} +\text{CH}_3 \\ | \\ \text{N} \\ | \\ +\text{Cl} \end{array}$ ; the latter compound has been pre-

pared in this laboratory by the late Isabella Vosburgh<sup>5</sup> and found *not* to undergo rearrangement. Now, the possibility of the existence of *electromers* was recognized by J. J. Thomson<sup>6</sup> as a consequence of the ap-

<sup>1</sup> Stieglitz and Leech, *loc. cit.*

<sup>2</sup> The electronic interpretation is given in detail, p. 285, *loc. cit.*

<sup>3</sup> Our theory will be taken in its broadest sense, as including the intermediate formation of univalent or bivalent nitrogen and univalent oxygen derivatives, etc.

<sup>4</sup> These will include the more recent and especially important observations of Kuhara, *loc. cit.*

<sup>5</sup> THIS JOURNAL, 38, 2081 (1916).

<sup>6</sup> Cf. "Corpuscular Theory of Matter," 1907, p. 131.

plication of the electron theory to chemical valence and structure, and a number of other writers<sup>1</sup> have applied his ideas to specific cases and found definite *indications* of the existence of electromers in equilibrium. As to the separate existence of electromers, W. A. Noyes,<sup>2</sup> in an important investigation of electromerism in the case of nitrogen chlorides, has found experimental indications, but no final proof, of such a relation. Convincing evidence of the separate existence of electromers has been uncovered by L. W. Jones<sup>3</sup> in a brilliant critical review of the chemistry of hydroxylamine derivatives. For the critical consideration of the consequences which would follow from the postulated relation between the electromers A and B and especially of the question whether they necessarily must be convertible into each other, it will be best to discuss in a few words the fundamental relations that must exist between electronic isomers.

Theoretically considered,<sup>4</sup> when one electromer is changed into another, a transfer of electrons between atoms contained in the same molecule occurs—that is, we have a case of intramolecular oxidation and reduction of atoms. This, if reversible, should be subject to the same laws that hold for reversible intermolecular oxidations and reductions, notably to the law of equilibrium. As is well known, such a condition of equilibrium may be almost, although not quite, one-sided (as in  $2\text{Fe}^{++} + \text{Cl}_2 \rightleftharpoons 2\text{Fe}^{+++} + 2\text{Cl}^-$ ) or it may involve a reaction that is to a distinct extent reversible (as in  $2\text{Fe}^{++} + \text{I}_2 \rightleftharpoons 2\text{Fe}^{+++} + 2\text{I}^-$ ).<sup>5</sup> Similarly, we must expect cases of electromerism, in which one electromer would be extraordinarily stable and the other capable of existence only in traces; in other instances, we should have electromers, for which “the oxidation-reduction constants”<sup>6</sup> of the differently charged elements make possible the existence, in some quantity, of the two electromers side by side. In view of the tremendous mobility of electrons, the equilibria should establish themselves, as a rule, with enormous speed whenever the atoms, whose charges cause the electromerism, are directly linked with each other. When atoms, which cause electromerism, are not directly linked together, tolerably permanent separate existence of electromers seems to be possible, as is shown by the fact that the only electromers whose separate existence has been convincingly

<sup>1</sup> Fry, *THIS JOURNAL* (Proc.), 30, 34 (1908); *Z. physik. Chem.*, 76, 387 (1911); *THIS JOURNAL*, 36, 248 (1914), etc.; Falk and Nelson, *School of Mines Quarterly*, 30, 179 (1909); *THIS JOURNAL*, 32, 1637 (1910), etc.; L. W. Jones, *loc. cit.*; W. A. Noyes, *THIS JOURNAL*, 35, 767 (1913), and others.

<sup>2</sup> *Loc. cit.*

<sup>3</sup> *THIS JOURNAL*, 36, 1268 (1914).

<sup>4</sup> Cf. also the authors referred to above.

<sup>5</sup> Cf. Stieglitz, “Qualitative Analysis,” Vol. I; pp. 272–276.

<sup>6</sup> Constants comparable with electrolytic solution tension constants are referred to.

established are the hydroxylamines<sup>1</sup> of the general type,  $R_3N^+ \begin{smallmatrix} -OR \\ +OH \end{smallmatrix}$  and  $R_3N^+ \begin{smallmatrix} -OH \\ +OR \end{smallmatrix}$ , which belong to the second class. Indeed, their separate existence and comparative stability is apparently due to the very fact that the different distribution of charges, which causes the electromerism, relates to two radicals OH and OR (more exactly, to their oxygen atoms), *which are not directly linked together*. Further, the following vital fact which has hitherto been too readily ignored, must be taken into account with the first class of electromers, whose differently charged atoms are directly linked and which must be considered to be reversibly convertible into each other. We will represent this type briefly as  $X^+ -Y$ ,  $X^- +Y$ . The reversible reaction  $X^+ -Y \rightleftharpoons X^- +Y$  involves the transfer of *two* electrons and, if we use the ordinary conceptions of electronic valence (the older or original Thomson conceptions), this should lead through the migration, first, of a single electron, to an intermediate stage, where neither X nor Y would be charged with excess of positive or negative electricity; in other words, the usual valence force between the two atoms would be lacking and, consequently, *dissociation into X and Y should take place*. The only alternative to this conclusion, which has apparently been entirely overlooked in the assumptions of electromeric relations before this, is that in the intermediate product  $X \ Y$ , *nonpolar valences*, of the type suggested by Bray and Branch,<sup>2</sup> G. N. Lewis,<sup>3</sup> Thomson,<sup>4</sup> and A. L. Parsons,<sup>5</sup> unite X and Y.<sup>6</sup> Indeed, the evident absence of such dissociation in indicated cases of electromerism would, if electromerism and nondissociation were proved beyond a doubt, be excellent chemical evidence in favor of the existence of some form of nonpolar valences. The well-known specific and generally one-sided actions of absorption, metathesis, etc., which are obviously *directed* by the nature of the specific *polar* charges on atoms both in inorganic and organic compounds, would find their explanation in the fact that *the chemically active molecules are those whose reacting atoms have polar charges*.<sup>7</sup>

On the basis of these general considerations concerning the relations

<sup>1</sup> Jones, *loc. cit.*

<sup>2</sup> THIS JOURNAL, 35, 1440 (1913).

<sup>3</sup> *Ibid.*, 35, 1448 (1913); 38, 762 (1916).

<sup>4</sup> *Phil. Mag.*, 27, 784 (1914).

<sup>5</sup> Cf. "A Magnetron Theory of the Structure of the Atom," Vol. 65, No. 11, Smithsonian Collections. On p. 30, such an intermediate phase is considered.

<sup>6</sup> Cf. Falk and Nelson, THIS JOURNAL, 36, 209 (1914); W. A. Noyes, *Ibid.*, p. 214; R. F. Brunel, *Ibid.*, 37, 709 (1915); Stieglitz, *Proc. Nat. Acad. Sci.*, 1, 196 (1915).

<sup>7</sup> Cf. Bray and Branch, Lewis, Thomson, Parsons, *loc. cit.*

of electromers, Compound A,  $R_3C + \begin{array}{c} +CH_3 \\ | \\ \text{---}N\text{---} \\ | \\ + \\ | \\ -Cl \end{array}$ , which, according to the

univalent nitrogen theory would be the rearranging univalent nitrogen salt in the rearrangement of triphenylmethyl- $\beta$ -methylhydroxylamine,  $(C_6H_5)_3C.N(CH_3)OH$ , by phosphorus pentachloride, and Compound B,

$R_3C + \begin{array}{c} +CH_3 \\ | \\ \text{---}N\text{---} \\ | \\ -Cl \end{array}$ , which Miss Vosburgh found to be nonrearranging, would,

as far as composition is concerned, seem to be electromers of the first (XY) class. If this is their relation, one should expect them to be convertible into each other: then, either B should undergo the molecular rearrangement as a result of going over first into A, or A should be transformed, in part at least, into the stable electromer B—or both actions should take place. No indications of any such results have been observed.<sup>1</sup> It still remains possible—or, indeed, probable—that the *fifth* (positive<sup>2</sup>) valence of nitrogen which enables ammonium radicals to combine with anions and form salts, and which also holds the chlorine in compound A in the *salt* form, is of a different character, in regard to its position in the atom or some other relation, from the remaining four valences, and not capable of going over electromerically into one of these other (negative) valences. In that event, the two electromers would really belong to the second group of electrômeric substances, of which the hydroxylamine derivatives, discovered by Jones and discussed above, are the best known representatives, and they would not necessarily be convertible into each other. The hydroxylamine electromers are themselves ammonium compounds, in which the valence in question is concerned.

On the whole, however, interpretations of the rearrangement that can do without assumptions concerning electromeric substances, must, for the present, be considered the more conservative. For this reason, the proved rearrangement of triphenylmethyl- $\beta$ -methylhydroxylamine should at the present moment be judged as weighty, although not conclusive, evidence in favor of Beckmann's view, that these rearrangements take place by a direct exchange of radicals.

2. The relation of stereoisomeric ketoximes to the products of their rearrangement (see Equation 4) still remains as indicated in the earliest report by one of us on his own theory,<sup>3</sup> an important, although not conclusive, fact, weighing in favor of Beckmann's view. It *may* find its ex-

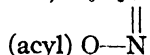
<sup>1</sup> Further work is suggested by these considerations.

<sup>2</sup> This valence is indicated by heavy type as  $\text{+}$  in the above formula for A.

<sup>3</sup> Stieglitz, *Am. Chem. J.*, 18, 754 (1896); *THIS JOURNAL*, 36, 277 (1914).

planation in the theory of a univalent nitrogen salt derivative, undergoing rearrangement, as discussed in detail in a previous paper by the one of us.<sup>1</sup> But such an interpretation is open to the same objections as raised by us in the previous paragraph against the salt theory, and, consequently, at present the relation of stereoisomerism to the rearrangement still remains important evidence in favor of a rearrangement by direct exchange of radicals.

3. A number of observations made by Kuhara<sup>2</sup> in a series of admirable investigations seem, at the first glance, to weigh heavily in the scales in favor of Beckmann's views. Among these facts we have as a most notable one, that syn-acetylethylbenzhydroxamic ester,  $C_6H_5C.OC_2H_5$ , is re-



arranged when it is heated for some time above its melting point.<sup>3</sup> The anti-derivative is not rearranged.<sup>4</sup> Kuhara formulates the rearrangement of the syn-derivative essentially in the way Beckmann would (Equation 4), but he also emphasizes the effect of the strength of the acid of the acyl radical attached to the oxygen of the oxime group on the ease with which the rearrangement takes place—a most important contribution to the subject. Further, it is characteristic, as Kuhara found, that the rearrangement of syn-acetylethylbenzhydroxamic ester, as well as that of the analogous acetyl derivative of benzophenone oxime,  $(C_6H_5)_2C:NO(\text{Acyl})$ , is *accelerated* by the presence of hydrogen chloride as a "catalytic agent," the velocities of rearrangement being found proportional to the concentration of acid present. Since acids act as "catalyzers" most commonly by salt formation, it is altogether likely that the rearranging substances, in the experiments with solutions, are the salts<sup>5</sup> of the acyl esters, rather than the esters themselves.<sup>6</sup> It is not at all impossible that, similarly, salts formed by the presence of traces of free acid should also be the active components even in the rearrangement by fusion. As a matter of fact, Kuhara found it impossible to rearrange the acetyl ester of benzophenoneoxime "by itself, even by the rise of temperature." It is always necessary to use hydrogen chloride as a catalytic agent. He ascribes this to the "weak negative character<sup>7</sup> of the acetic acid residue." In support of this view, he brings the important observation that the

<sup>1</sup> Stieglitz and Leech, *loc. cit.*, p. 281.

<sup>2</sup> *Loc. cit.*

<sup>3</sup> *J. Chem. Soc.*, 106, 538 (1914).

<sup>4</sup> Cf. Werner, *Ber.*, 25, 33 (1892); 26, 1652 (1893); 29, 1153 (1896).

<sup>5</sup> The question of the ionization of these salts is not considered here.

<sup>6</sup> Kuhara proposed this view for the rearrangement of acetylbenzophenoneoxime by hydrogen chloride [*Mem. Coll. Sci. Kyoto*, 1, 25 (1914)].

<sup>7</sup> *Loc. cit.* As a matter of fact, in these hydroxylamine derivatives we really have the unstable positive radical  $CH_3CO.O^+$  (see below).

benzenesulfonyl ester of benzophenone oxime, "owing to the presence of the strong negative acid residue," undergoes the rearrangement apparently spontaneously, without the need of a catalyzing acid, slowly in the cold, very rapidly when it is heated above its melting point of  $62^{\circ}$ . This whole evidence is open to quite another interpretation: it would seem as if the acetyl derivatives might not rearrange spontaneously on account of the fact that any traces of acetic acid, formed by the action of moisture on the ester, might be too weak to form a salt in sufficient quantity with the oxime ester, and in the absence of the salts, there would be no rearrangement; but any traces of benzene sulfonic acid, so liberated, could act autocatalytically, since the acid would be strong enough to form a salt with the ester. It would be important to determine whether the spontaneous rearrangement of the sulfonyl ester would not be *accelerated* by the presence of hydrogen chloride.<sup>1</sup> Beyond suggesting that the hydrochloric acid helps out the weak acetic acid residue in its tendency to exchange positions with the phenyl radical, Kuhara does not explain how the formation of the hydrochlorides of the acetyl derivatives should facilitate the rearrangement. Two explanations suggest themselves: one, obviously, is that *the apparent necessity for the formation of a rearranging salt* would be in excellent agreement with the view that a salt of a univalent nitrogen derivative is the *real rearranging component in these reactions*<sup>2</sup> and that the rearrangement does not proceed until salt formation gives the molecule its only opportunity to form any univalent nitrogen derivative. Kuhara's view that the "weak negative character of the acetic acid residue" is responsible for the nonrearrangement of acetyl benzophenoneoxime without the aid of hydrochloric acid seems to be contradicted by the peculiar fact that all attempts to rearrange chloroimido-benzophenone,  $(\text{C}_6\text{H}_5)_2\text{C}:\text{NCl}$ , have failed to indicate the least trace of a rearrangement;<sup>3</sup> the hydride corresponding to the radical Cl is hydrogen chloride itself,<sup>4</sup> an acid fully as strong as, or stronger than, benzene-

<sup>1</sup> Since this was written, Mr. Sidney Cadwell has investigated this question for me and found that added acid (hydrogen chloride, benzene sulfonic acid) does decidedly *accelerate* the rearrangement of the benzene sulfonic acid ester of benzophenone oxime, but he has also found that there is a slow, spontaneous rearrangement of the ester itself even at  $0^{\circ}$  and even in the presence of a weak base like pyridine (cf. Kuhara). This result will be published later in detail.—J. S.

<sup>2</sup> The equation representing the rearrangement from this point of view is given by Stieglitz and Leech, *loc. cit.*, p. 281.

<sup>3</sup> Heat, bases, chlorine, phosphorus pentachloride have been tried. Kuhara's work suggests a further trial with *acids* and this will be undertaken. (Since this was written, Henry R. Curme has studied the action of concentrated sulfuric acid on the chloroimide: no trace of a rearrangement product could be found, under exactly the same conditions of work as led to a rearrangement of benzophenoneoxime.)

<sup>4</sup> Kuhara takes no account of the positive charges on the radicals  $\text{CH}_3\text{CO}\cdot\text{O}^+$  and  $\text{C}_6\text{H}_5\text{SO}_3\cdot\text{O}^+$  in the oxime esters (Stieglitz and Leech, *loc. cit.*) and contrasts the



sulfonic acid. Acid decomposes the chloroimide and hence salts, when formed, decompose in another way than by rearrangement, and it is certainly significant that just in this case we cannot secure a rearrangement of the free chloroimide itself. It seems possible, therefore, that Kuhara's interesting results, from which we can recognize the importance of salt formation with acids for the rearrangements of oximes and their esters, may really signify that the easiest path for these rearrangements is over univalent nitrogen compounds, *including their salts*, and that a direct exchange of radicals is a much more difficult process.

We wish to point out, however, that the major role played by salt formation in the rearrangement of the oxime esters may consist not simply in making possible or facilitating the formation of a univalent nitrogen compound, but may well be a further instance of what seems to be a broad and fundamental principle, namely that *acids are found to facilitate changes and migrations of unstable positive atoms or radicals*,<sup>1</sup> *which in their migration or change go over into their stable negative forms*. Besides the cases just discussed, we find this principle applying to the various forms of rearrangement of hydrazines with the unstable atom  $+N^{\cdot}$ ,<sup>2</sup> such as  $C_6H_5HN^{\cdot} + NHC_6H_5$  (e. g., the rearrangement into benzidine with the stable atoms  $-N^{\cdot}$ ), applying to the rearrangement of phenylhydroxylamine,<sup>3</sup>  $C_6H_5HN^{\cdot} + OH^{\cdot}$ , with the unstable atom  $+O^{\cdot}$ , into amino phenols<sup>4</sup>  $HO^{\cdot} + C_6H_4.NH_2$ , with the stable atom  $-O^{\cdot}$ , of acylhalogenanilides<sup>5</sup>  $RCO.N(Cl^+)C_6H_5$ , with the unstable atom  $Cl^+$ , to acylchloroanilides  $RCO.NHC_6H_4Cl^{\cdot}$ , with the stable atom  $Cl^{\cdot}$ , which are all accomplished or accelerated with the aid of acids: *all involve the change* strength of the hydrides of the radicals, namely, acetic and benzenesulfonic acids. This is why HCl and not HOCl is used in the text for purposes of comparison. As a matter of fact, the real acids, of which the compounds may be said to be derivatives for the purposes of comparison, are the per-acids  $CH_3CO_2^{\cdot}O^+OH$ ,  $C_6H_5SO_3^{\cdot}O^+OH$ , and hypochlorous acid  $Cl^+OH$ .

<sup>1</sup> The result of the migration is always a stronger and more stable base and the effect of the acid is, therefore, in agreement with the energy relations that must be involved. Probably potential relations of the unstable positive forms of the elements, akin (*mutatis mutandis*) to solution tensions, are favorable to their transformation in acid media into the stable negative forms of the elements. Investigations from this point of view are greatly to be desired.

<sup>2</sup> Stieglitz and Curme, *Ber.*, 46, 911 (1913).

<sup>3</sup> Stieglitz and Leech, *loc. cit.*

<sup>4</sup> Bamberger, *Ber.*, 33, 3600 (1900); 34, 1 (1901).

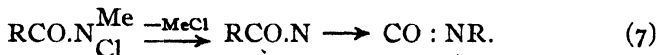
<sup>5</sup> Stieglitz and Slosson, *Ber.*, 28, 3265 (1895); Armstrong, *J. Chem. Soc.*, 77, 1047 (1900); Acree and Johnson, *Am. Chem. J.*, 38, 265 (1907), who brought evidence indicating that the salts are the rearranging components. These chemists did not discriminate between positive and negative halogens in these compounds. See also Orton, *J. Chem. Soc.*, 95, 1456 (1909).

of unstable positive, to stable negative, atoms.<sup>1</sup> Underlying all of these rearrangements is the tendency of these unstable atoms to absorb electrons: and they thus disturb, *eo ipso*, the valence relations in a molecule and the rearrangements are necessary sequels.<sup>2</sup>

II. We will turn now to the consideration of the most important facts which appear to favor the view that unsaturated (primarily univalent, possibly also bivalent<sup>3</sup>) nitrogen derivatives are intermediate products in the rearrangements of the various classes of compounds which suffer this typical rearrangement, such as the hydroxylamines, the halogenamines, the azides.

1. By losing nitrogen, the azides,  $\text{RCO.N}_3$ ,  $\text{R}_3\text{C.N}_3$ , rearrange and give exactly the same products as do the other classes of compounds discussed. Recently, in this laboratory, Senior<sup>2</sup> found that  $(\text{ClC}_6\text{H}_4)(\text{C}_6\text{H}_5)_2\text{C.N}_3$ , even gives the same proportion of aniline and chloroaniline in the rearrangement as does  $(\text{ClC}_6\text{H}_4)(\text{C}_6\text{H}_5)_2\text{C.NHOH}$ . A "direct exchange" of nitrogen with the radical R,  $(\text{C}_6\text{H}_5)$  or  $(\text{ClC}_6\text{H}_4)$  seems out of the question.

2. When univalent nitrogen derivatives can be formed readily, we have smooth reactions, proceeding at low temperatures, in marked contrast with those cases where univalent nitrogen cannot be obtained readily and, at best, only indirectly: (a) Dry salts of acylchloroamides rearrange explosively when warmed gently,<sup>4</sup> and in solution the salts rearrange rapidly at low temperatures.



In contrast with this behavior we find that alkyl derivatives,  $\text{RCO.NCl}(\text{CH}_3)$ , do not rearrange<sup>5</sup> and none of the chloroimidoesters,  $\text{RC}(\text{:NCl})\text{OCH}_3$ , which have been obtained in syn and antistereoisomeric forms corresponding to those of the hydroxamic esters, is rearranged, until destructive distillation is resorted to, in which the methyl group is lost.<sup>6</sup> According to the univalent nitrogen theory of the one of us, these results are to be expected, but they cannot be explained without further specific assumptions on the basis of the Beckmann theory of direct exchanges, since there is no apparent reason why there should not be an equally ready direct exchange of the radical R and the (positive) chlorine atom in these cases and in the non-alkylated compounds. (b) The dry

<sup>1</sup> Miss De Sale is investigating the question to what extent acids accelerate the rearrangement of azides. The rearrangement of peroxides by acids will also be studied from this point of view.

<sup>2</sup> *Proc. Nat. Acad. Sci.*, **1**, 207 (1915).

<sup>3</sup> Stieglitz and Leech, *loc. cit.*

<sup>4</sup> Unpublished work with O. Eckstein.

<sup>5</sup> Slosson, *Am. Chem. J.*, **29**, 289 (1903).

<sup>6</sup> Unpublished work with Earle and W. J. Hale.

metals salts of dihydroxamic acids<sup>1</sup> also rearrange spontaneously and explosively at room temperatures, forming isocyanates (see Equation 2). The corresponding esters,  $\text{RC}(\text{OC}_2\text{H}_5) : \text{NO} \cdot \text{COCH}_3$ , rearrange very slowly, if at all, and then only at elevated temperatures. Their salts with acids rearrange much faster and may even be present in all of their rearrangements (see I, 3 above) and these salts may produce univalent nitrogen derivatives. (c) Triphenylmethyldichloroamine,  $(\text{C}_6\text{H}_5)_3\text{C} \cdot \text{NCl}_2$ , is readily rearranged by heat<sup>2</sup> with loss of chlorine; triphenylmethylbromoamine,  $(\text{C}_6\text{H}_5)_3\text{C} \cdot \text{NBr}$ , is likewise readily rearranged when heated with alkali with a loss of hydrogen bromide; but triphenylmethylchloromethylamine,  $(\text{C}_6\text{H}_5)_3\text{C} \cdot \text{NClCH}_3$ , is not rearranged by heat, by alkali, or, even by destructive distillation.<sup>3</sup> Chloroimidobenzophenone,  $(\text{C}_6\text{H}_5)_2\text{C} : \text{NCl}$ , has resisted every effort to effect its rearrangement and the same is true of the stereoisomeric chloroimides,<sup>4</sup>  $(\text{C}_6\text{H}_5)(\text{XC}_6\text{H}_4)\text{C} : \text{NCl}$ . If the theory of direct exchange were correct, these substances, above all others, should show a spontaneous exchange of the aryl and halogen radicals. It is true, however, that it is still possible that the favorable medium has not yet been discovered for effecting the rearrangement of these compounds.

3. As has often been pointed out by the one of us, the reagents used to effect the different varieties of rearrangement are the very ones which we would select in attempting to obtain univalent nitrogen derivatives as intermediate products: Bases for the acyl halogenamides,  $\text{RCO} \cdot \text{NH}(\text{Hal})$ , for dibenzhydroxamic acids,  $\text{RCO} \cdot \text{NH}(\text{OCOR})$ , for triphenylmethyl-halogen amines,  $\text{R}_3\text{C} \cdot \text{NH}(\text{Hal})$ , for benzoyltriphenylmethylhydroxylamine,<sup>5</sup>  $\text{R}_3\text{C} \cdot \text{NH}(\text{OCOC}_6\text{H}_5)$ ; acid dehydrating agents for oximes,  $\text{R}_2\text{C} : \text{NOH}$ , for hydroxylamines,  $(\text{C}_6\text{H}_5)_3\text{C} \cdot \text{NHOH}$  and  $(\text{C}_6\text{H}_5)_3\text{C} \cdot \text{N}(\text{CH}_3)\text{OH}$ , phosphorus pentoxide for the hydrochloride,  $(\text{C}_6\text{H}_5)_3\text{C} \cdot \text{NHOH} \cdot \text{HCl}$ ; heat for acylazides,  $\text{RCO} \cdot \text{N} \cdot \text{N}_2$  (with loss of nitrogen), for triphenylmethylazides,<sup>6</sup>  $\text{R}_3\text{C} \cdot \text{N} \cdot \text{N}_2$ , for triphenylmethyldichloroamine,  $(\text{C}_6\text{H}_5)_3\text{C} \cdot \text{NCl}_2$  (chlorine being lost). To these cases may now be added the apparent necessity of using a catalyzing acid for the rearrangement of the acetyl ester of benzophenone oxime<sup>7</sup> (see I, 3 above), the very agent required to make a univalent nitrogen derivative possible.

<sup>1</sup> L. W. Jones, *Am. Chem. J.*, **48**, 1 (1912).

<sup>2</sup> Isabella Vosburgh, *THIS JOURNAL*, **38**, 2081 (1916).

<sup>3</sup> Stieglitz and Vosburgh, *Ber.*, **46**, 2151 (1913).

<sup>4</sup> Peterson, *Am. Chem. J.*, **46**, 325 (1911).

<sup>5</sup> In the article by Stieglitz and Leech doubt was expressed about the position of the benzoyl group on account of the inability of the benzoate to form a salt (*loc. cit.*, p. 292). Difficulty in salt formation has now been found to be common in the triphenylmethyl derivatives we are studying. The absence of the ferric chloride test for an OH group makes the above structure probable.

<sup>6</sup> J. K. Senior and Stieglitz, *Proc. Nat. Acad. Sci.*, **1**, 207 (1915).

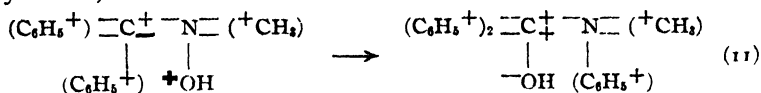
<sup>7</sup> Kuhara, *loc. cit.*



rangements produced by the action of an electric current on the salts of organic acids. The fundamental analogy of the resulting changes to the rearrangements of the nitrogen derivatives under discussion has already been pointed out by the one of us.<sup>1</sup>

III. If one considers the evidence in I and II, one must be impressed by the fact that certain facts are more simply interpreted on the basis of Beckmann's theory of a direct exchange of radicals, that still other facts are quite incompatible at present with Beckmann's views and in striking agreement with the intermediate product theory of the one of us. Common to both views and *the most important fact in any theory of the rearrangements, is that the latter originate from the presence of unstable positive atoms,  $Cl^+$ ,  $-O^+$ ,  $\equiv N^+$ , in the molecules of the compounds in question, and these atoms, by satisfying their tendencies to absorb electrons and form the common, stable, negatively charged atoms, disturb the valences which hold all atoms in the structure of the molecules and start the rearrangement into stable molecules.*<sup>2</sup> From this point of view, it must be evident that *both* forms of rearrangement might well be possible, one by a direct exchange, the other by way of a dissociation into unsaturated radicles. The question of the mechanism of the rearrangements resolves itself then largely into a question of the path followed by the migrating electrons. For these reasons it seems desirable to analyze, as briefly as possible, the electronic interpretations of the rearrangements from the different points of view: they bring out their relations more precisely than do the structural considerations alone and they point the direction for further experimentation.

A. The electronic interpretation of Beckmann's assumption of a direct exchange of radicles has never been presented, we believe. In illustration of it, we have for the rearrangement of β-triphenylmethyl-β-methyl hydroxylamine,<sup>3</sup>



The shifting charges are indicated by heavy type.

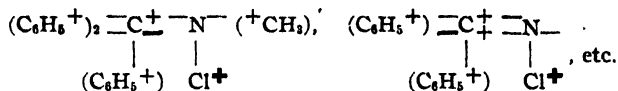
Characteristic of this theory, evidently, is that the unstable positive radical  $+OH$  secures its electrons *directly* from the carbon atom of the triphenylmethane nucleus, an exchange of radicals (the new negative  $-OH$  and the positive phenyl radical) occurring practically simultaneously with this shifting of electrons. This mode of expression brings out in the most striking fashion some of the most important objections to Beck-

<sup>1</sup> Stieglitz and Leech, *loc. cit.*, p. 281.

<sup>2</sup> Stieglitz, *Proc. Nat. Acad. Sci.*, 1, 207 (1915). See also L. W. Jones, *loc. cit.* and Stieglitz and Leech, *Ibid.*

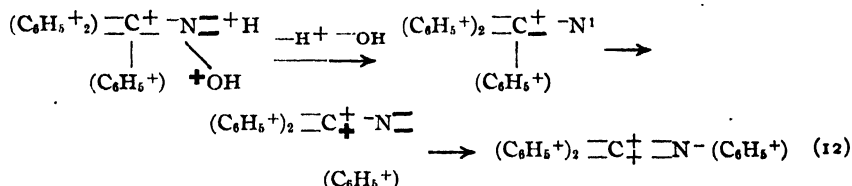
<sup>3</sup> In place of  $+OH$  we may put its acyl derivatives,  $RCO.O^+$ .

mann's theory: it fails utterly to explain why we have no rearrangements of compounds strictly analogous to the above, such as



In these nonrearranging compounds the tendency for the exchange of electrons should be even greater than in the preceding rearranging compound, if we judge by comparing the activity of (positive) chlorine in chloroamines and hypochlorites with that of (positive) oxygen in such a substance as hydrogen peroxide.

B. According to the univalent nitrogen theory of the rearrangements, we should have, for instance, for triphenylmethylhydroxylamine:



The characteristic feature of this theory is that the unstable positive element secures its electrons from the nitrogen to which it is attached, by capturing two of its valence electrons. One of these two available electrons attached to the nitrogen in the original molecule is the one holding the positive radical itself (here  $^+\text{OH}$ ), the other is taken from the nitrogen only if it holds hydrogen, a metal (either may be ionized or non-ionized) or some other easily displaced atom, *but it is not available when it holds an alkyl group or its equivalent*.<sup>2</sup>

*In turn*, the unsaturated nitrogen, comparable with an element like fluorine,<sup>3</sup> secures from the carbon atom, to which it is attached, two electrons again, the rearrangement following as a result. This view explains the very facts which the Beckmann theory fails utterly to explain: thus, in  $(\text{C}_6\text{H}_5^+)_3 \text{—} \text{C}^+ \text{—} \text{N}^- (\text{Cl}^+) (\text{CH}_3)^+$ , the nitrogen has only one readily

<sup>1</sup> It was originally considered (Stieglitz and Leech, *loc. cit.* and Jones, *Ibid.*) that in the univalent nitrogen derivative the nitrogen might have the structure  $\text{—} \text{N}^+ \text{—}$  in place of  $\text{—} \text{N} \text{—}$ . The latter was given the preference by the one of us. Below, under C, additional reasons for distinguishing sharply between the two closely related forms will be brought.

<sup>2</sup> Similarly, in  $(\text{H}^+)_2 \text{—} \text{S}^-$ , the  $\text{—} \text{S}^-$  is very easily deprived by oxidizing agents of both its electrons, but in  $(\text{CH}_3^+) \text{—} \text{S}^- \text{—} \text{H}$  it is deprived only of the electron holding the hydrogen atom. This is most likely due to the fact that the ions,  $\text{HS}^-$ ,  $\text{S} = \text{CH}_3 \text{S}^-$ , with exposed electrons, are the components, which are most easily deprived of these electrons (cf. Stieglitz, "Qualitative Analysis," Vol. I, Chapters XIV and XV). Possibly, too, the union with  $\text{CH}_3$  is of the nonpolar type.

<sup>3</sup> Stieglitz and Leech, *loc. cit.*

available<sup>1</sup> electron, not the two necessary for the formation of a univalent nitrogen derivative and no rearrangement occurs. On the other hand, the present view does not explain, without further assumptions (see p. 2051) the rearrangement of  $\beta$ -triphenylmethyl- $\beta$ -methyl hydroxylamine.

Now, the *force* with which electrons would be drawn by the unstable positive atom from another atom in the same molecule must depend on at least two factors, namely a tension factor measuring the intensity of the selective tendency with which each element holds or seeks to absorb electrons—comparable with the solution tension of the free elements—and secondly, on the distance separating the atoms between which a transfer of electrons may occur. As to the tension factors in all of these rearrangements, the final products prove beyond question that these factors must favor the gain of electrons by the unstable positive element at the expense of the *carbon* atom holding the nitrogen. In other words, the carbon must lose two electrons, as far as tension is concerned, more readily than the nitrogen; otherwise the univalent nitrogen derivative would be tolerably stable. Consequently, unless the direct migration of electrons from the carbon to the unstable positive element is obstructed by virtue of the important factor of distance and intervening atoms, as far as the tension factor is concerned, *the direct migration would be the natural path for the transfer of electrons*. Instances of such direct migration under favorable conditions might therefore not be unexpected (see A).

But, further, the important factor of distance unquestionably must favor the absorption of electrons first from the nitrogen by the unstable positive element, which is in direct union with it; the nitrogen can then recover its electrons from the carbon with which it is in direct union. This probably is the reason why *the path of least resistance* to the rearrangements<sup>2</sup> seems to be over the univalent nitrogen products and why certain compounds, which have the necessary instability of charges, do not rearrange, when the path over the univalent nitrogen is blocked. This mechanism has the advantage therefore of having *both* factors, which control the movement of electrons, leading to the final readjustment.

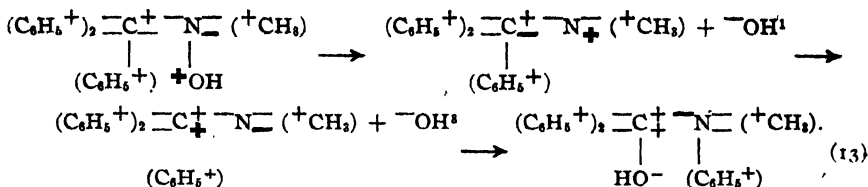
It seems especially important, from these considerations, to subject the nonrearranging compounds to a still more searching experimental investigation, in order to determine whether the path toward a rearrangement really is altogether blocked.

C. There is a third electronic interpretation<sup>3</sup> of the rearrangements, which contains in it elements of both of the preceding interpretations; we may have a dissociation, preceding the exchange of radicals.

<sup>1</sup> The union with  $\text{CH}_3$  may even be of the nonpolar type, if such valences should be found to exist.

<sup>2</sup> Stieglitz and Vosburgh, *Ber.*, **46**, 2149 (1913).

<sup>3</sup> Cf. Stieglitz and Leech, *loc. cit.*, and L. W. Jones, *Ibid.*



This interpretation would labor under the same difficulties as the theory of Beckmann (see A) in accounting for the nonoccurrence of rearrangements of certain halogen derivatives (see A) and would have the added difficulty that the factor of proximity would be no obstruction to a similar rearrangement in this case. It should be borne in mind for those rearrangements which seem to take place without the intermediate formation of a univalent nitrogen derivative.<sup>2</sup>

Our conclusions may be summarized as follows:

1. Unless conclusive evidence is brought that *salts* leading to the intermediate formation of salts of univalent nitrogen derivatives, are involved in their rearrangement, the rearrangement of  $\beta$ -triphenylmethyl- $\beta$ -methylhydroxylamine, established in this paper, the relation of stereoisomerism of oximes to their rearrangement products, established by Beckmann, Werner and Kuhara, and also the spontaneous rearrangement of the sulfonic ester of benzophenone-oxime, observed by Kuhara, would be inconsistent with the theory of the intermediate formation of univalent nitrogen derivatives in the rearrangement of hydroxylamines and at present these facts agree better with Beckmann's theory of a direct exchange of radicals or with a modification of this theory (see C, above). Intermediate salt formation, if established, would harmonize these facts with the univalent nitrogen theory.

2. Other facts, such as the rearrangements of azides and especially also the nonrearrangement of chloroimidobenzophenones, of chloroimidoesters, and of  $\beta$ -triphenylmethyl- $\beta$ -methylchloroamine, are inconsistent, without further specific assumptions, with Beckmann's theory of a direct exchange of radicals, but are in striking agreement with Stieglitz's theory of the intermediate formation of unsaturated nitrogen derivatives in the rearrangements of chloroamines, hydroxylamines, and azides.

3. Unless further experimentation should modify these facts or their bearing, one should consider that both types of rearrangement may take place.

4. Common to both theories and the most important feature in their modern forms is that the rearrangements originate from the tendency of unstable positive atoms,  $\text{Cl}^+$ ,  $\text{O}^+$ ,  $\text{N}^+$ , etc., to go over into their

<sup>1</sup> Or some equivalent ion, such as  $\text{Cl}^-$ ,  $\text{C}_6\text{H}_5\text{SO}_3^-$ , etc.

<sup>2</sup> Other variations of this fundamental idea are possible.



stable negative forms,  $\text{Cl}^-$ ,  $\text{O}^-$ ,  $\text{N}^-$ , by a capture of electrons from other atoms in the same molecule a change which is effected in the rearrangements in question. It is quite consistent with this fundamental relation that the rearrangement should go over one or the other path, the one over the unsaturated nitrogen derivatives forming probably the path of least resistance.

5. The same fundamental cause, the charge on unstable atoms, with consequent shifting of electrons, underlies the rearrangement of peroxides, of hydrazines, of acylhalogenanilides, of aryl hydroxylamines, and similar compounds.

### Experimental Part.<sup>1</sup>

**The Rearrangement of Triphenylmethyl- $\beta$ -methylhydroxylamine,**  $(\text{C}_6\text{H}_5)_3\text{C}.\text{N}(\text{CH}_3)\text{OH}$ .—The method of Stieglitz and Leech<sup>2</sup> for preparing triphenylmethylmethylhydroxylamine hydrochloride was followed, but it was found better to purify this salt by washing it thoroughly with ligroin (b. p. 70–80°) than to crystallize it from a chloroform-ether solution. By the latter process there is always some dissociation into triphenylmethylchloride and methylhydroxylamine hydrochloride. The free base may also be extracted with ligroin instead of ether, as the base is quite soluble in it, and then the hydrochloride precipitated from the solution by the introduction of the dry acid gas.

The purity of the salt was determined by its melting point and by the analysis for the content of hydrogen chloride. The free base was prepared from it by treatment with alkali solution and extraction of the base with ether. The ether solution was dried with fused calcium chloride and the solvent evaporated. The base remaining was a very mobile, almost colorless liquid, which, without further purification, solidified, at once, when stirred with a glass rod. The solid melted at 106° and when it was once recrystallized from ligroin, it melted at 111°. Leech found 113° as the constant melting point, after prolonged recrystallization. The yield is good—5.5 g. were obtained from 9 g. of triphenylmethylchloride.

To rearrange the base, 3 g. of it were dissolved in 30–40 cc. of ether and 5 g. of phosphorus pentachloride added to the solution. The mixture stood at room temperature for 24 hours, during which time a slightly yellow coloration appeared. The coloration increased when the mixture was heated on an electric bath for four hours. After the heating, a strong ether solution (3 cc.) of hydrogen chloride was added to the mixture to insure the presence of an excess of the acid. The supernatant liquid was decanted through a filter and the residue washed well with ether.

<sup>1</sup> I take pleasure in giving expression to my grateful appreciation of the painstaking and skilful work of Mr. Stagner, who carried out the experimental work under my direction.—J. S.

<sup>2</sup> *Loc. cit.*

Water (20 cc.), containing hydrochloric acid, was now added to the residue and any trace of residue on the filter was washed into the flask with the larger residue. Some of this residue was insoluble in the dilute acid. The mixture was warmed an hour on the water bath. The insoluble residue melted but did not dissolve. The mixture was cooled and ether added to it. This dissolved the residue which was not soluble in the aqueous solution. The ether solution was separated and the water solution extracted twice again with ether. The ether extracts, containing benzophenone, was examined as described later on. The aqueous solution remaining was made alkaline, saturated with sodium chloride, and the free methyl aniline twice extracted with ether. The base was next twice extracted from the ether solution with 20 cc. of very dilute hydrochloric acid (0.5 *N*). The acid solution was filtered into a weighed beaker and the solution evaporated nearly to dryness on a steam bath and the last traces of moisture removed *in vacuo*. The residue (methyl-aniline hydrochloride) weighed 0.535 g.

A second rearrangement was similarly made in which a gram of the free base gave 0.151 g. of methylaniline hydrochloride. The theoretical yield is 0.496 g. methylaniline hydrochloride per gram of triarylmethyl-methylhydroxylamine.

**Identification of Methylaniline.**—The following tests proved the salt to be methylaniline hydrochloride:

1. A small quantity of the residue was dissolved in water and the solution made alkaline. Bleaching powder solution was added and gave the characteristic deep blue color, discovered by Leech as a test for methylaniline.<sup>1</sup>

2. A small quantity of the residue, when twice crystallized from dry chloroform by the addition of ether, melted at 119–122°. When these crystals were mixed with synthetic methylaniline hydrochloride they melted at the same temperature, 119–122°. Methylaniline hydrochloride, obtained from a redistilled Kahlbaum preparation, melted at 119–121°.

3. 0.1392 g. of the residue, which had been twice recrystallized from chloroform and ether, required 9.76 cc. of 0.1 *N* AgNO<sub>3</sub>, when analyzed by the Volhard method. Theoretical quantity for C<sub>7</sub>H<sub>10</sub>NCl, 9.70 cc.

4. A quantitative analysis of the chloroplatinate was made. The older literature<sup>2</sup> states that methylaniline chloroplatinate is unstable and darkens quickly, with decomposition. But this is erroneous. The chloroplatinate prepared from synthetic methylaniline hydrochloride forms a nice looking yellow precipitate which does not darken at all and which contains the theoretical quantity of platinum. After this fact

<sup>1</sup> THIS JOURNAL, 35, 1042 (1913).

<sup>2</sup> Graham-Otto-Kolbe, IIIa, 178 (1878).

had been determined, the methylaniline salt obtained from the rearrangement products was analyzed. About 0.22 g. of the hydrochloride, that had been once crystallized from chloroform and ether, was dissolved in 10-15 drops absolute alcohol. This solution was added to 0.4 g. of chloroplatinic acid dissolved in 15-20 drops of alcohol. The yellow precipitate of methylaniline chloroplatinate formed at once. The precipitate was transferred to a filter, washed first with 10-20 drops of alcohol, and then slowly with 30 cc. of a half and half mixture of absolute ether and alcohol. The solid was brought to constant weight *in vacuo* in an hour or two.

Subst. 0.3493 g. gave 0.1097 g. Pt.

Calc. for  $C_{14}H_{20}N_2PtCl_6$ : Pt, 31.27%. Found: Pt, 31.40%.

**Identification of Benzophenone.**—The ether solution of the benzophenone, which was extracted from the acid solution of the hydrolyzed products of the rearrangement, was freed from the ether by evaporation in a current of air. A red tinted very mobile liquid remained which weighed 0.611 g. This substance remained liquid for several days. Finally, when it was touched by a minute trace of pure benzophenone clinging to the rounded end of a melting point tube, it solidified at once. Some of it was twice crystallized from ligroin and melted at 46-47° and when it was mixed with pure benzophenone, it melted at 46.5-48°. Pure benzophenone melted at 47-48.5°.

**Triphenylcarbinol.**—The triphenylmethylmethylhydroxylamine did not rearrange quantitatively. This was shown by the fact that approximately 1.5 g. of triphenylcarbinol was obtained in addition to the aniline and benzophenone already described. A part of the base appeared to dissociate into triphenylmethylchloride and hydroxylamine, as observed by Stieglitz and Leech. The ether solution which had been decanted from the insoluble rearranged products was freed from ether by evaporation and the gummy residue remaining was hydrolyzed with alkali solution. The carbinol thereby produced was crystallized from ligroin and identified by its melting point.

**Rearrangement of  $\beta$ , $p$ -bromophenyldiphenylmethyl- $\beta$ -methylhydroxylamine,  $(BrC_6H_4)(C_6H_5)_2C.NCH_3OH$ .**— $p$ -Bromotriphenylmethylchloride was condensed with methyl hydroxylamine. The concentrations of solutions were the same as those used in the preparation of triphenylmethylmethylhydroxylamine. The solvents were evaporated and the gummy residue was extracted with ligroin,<sup>1</sup> (b. p. 70-80°). From this solution the hydrochloride of the base was precipitated by dry hydrogen chloride.

<sup>1</sup> Attempts were made to precipitate the hydrochloride from an ether solution but the salt is very soluble in ether and solidification cannot be obtained if ether is present. A few drops of ether added to the salt purified from ligroin softens it into a gum—probably due to the base being very weak and the salt being decomposed by the oxonium valences of the ether.

The salt separates out very white. It is quite insoluble in the ligroin but is soluble in chloroform, alcohol, and ether. It reduces boiling Fehling's solution, softens at  $70^{\circ}$ , but has no true melting point. The yield of the salt is good; 8 g. of it was obtained from 12 g. bromotriphenylmethylchloride. From its behavior it seems to be an unstable salt, easily losing its acid.

For analysis, it was placed in a flat crystallization dish and stirred in an atmosphere of dry hydrogen chloride and then placed in a desiccator over potassium hydroxide and left in an ice chest for five days. Analysis for the content of the hydrochloric acid was then made by titration with 0.1 *N* KOH. The salt was dissolved in 25 cc. of absolute alcohol and ten drops of phenolphthalein indicator used. It required 0.06 cc. of alkali to correct for  $\text{CO}_2$  in the alcohol.

Subst. 0.2437, 0.1950; cc. 0.1 *N* KOH, 6.12, 4.88.

Calc. for  $(\text{BrC}_6\text{H}_4)(\text{C}_6\text{H}_5)_2\text{CNCH}_2\text{OH}\cdot\text{HCl}$ : HCl, 9.01. Found: 9.16, 9.12.

The salt was next left *in vacuo* at room temperature over sticks of potassium hydroxide for three days. It then showed 92% of the calculated amount of hydrogen chloride. The salt evidently is not stable and dissociates slowly at room temperature into the free base and free hydrogen chloride.

**Rearrangement of *p*-Bromophenyldiphenylmethyl- $\beta$ -methylhydroxylamine.**—The base,  $(\text{BrC}_6\text{H}_4)(\text{C}_6\text{H}_5)_2\text{CNCH}_2\text{OH}$ , was obtained from its hydrochloride by treatment of the latter with alkali solution and extraction with ether. The ether solution was freed from moisture by means of fused calcium chloride. The solvent was then evaporated, leaving a liquid substance. Some of this liquid (2.25 g.) was dissolved in 30–40 cc. of ether and phosphorus pentachloride (4 g.) was added to the solution. The mixture was heated on an electric bath for four hours. After the heating, 3 cc. of ether containing hydrogen chloride was added, and the supernatant liquid poured from the insoluble yellow colored compounds. The insoluble substance was washed twice with 15 cc. of ether. The residue was hydrolyzed and the ketones (benzophenone and bromobenzophenone) and the aniline salts (the hydrochlorides of methylaniline and methyl bromoaniline) were isolated exactly as they were in the case of the rearrangement of triphenylmethylmethylhydroxylamine.

The base (2.25 g.) yielded 0.172 g. of mixed aniline hydrochlorides and 0.301 g. of the two ketones, benzophenone and bromobenzophenone. A second rearrangement of 1.6 g. of base gave 0.111 g. of the mixed aniline salts.

A trace of the hydrochlorides, when made alkaline and treated with bleaching powder solution, gave a navy blue color, the test for methyl aniline (methylbromoaniline does not give this color test). Another small quantity of the aniline salts was freed from the hydrochloric acid and precipitated from ether solution by means of oxalic acid. This oxalate showed the presence of halogen when tested with copper oxide in Bunsen flame.

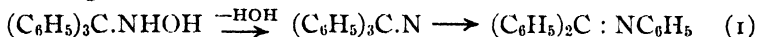
[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

## THE MOLECULAR REARRANGEMENT OF TRIARYLMETHYL-HYDROXYLAMINES.

BY BERT ALLEN STAGNER.<sup>1</sup>

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That the hydroxylamine derivatives of triphenylmethane undergo a rearrangement entirely analogous to the Lossen rearrangement of hydroxamic acids and the Beckmann rearrangement of oximes and under exactly similar conditions, was shown by the work of Stieglitz, Reddick and Leech.<sup>2</sup> The rearrangement is effected by the action of phosphorus pentachloride on the hydroxylamine derivative or by the action of phosphorus pentoxide on the hydrochloride of the base.<sup>3</sup> The product of the rearrangement is a phenylimidobenzophenone. According to the theory of Stieglitz<sup>4</sup> the action is formulated as follows:



When a substituting group replaces hydrogen in one or more of the phenyl groups, as in  $(\text{XC}_6\text{H}_4)(\text{C}_6\text{H}_5)_2\text{C.NHOH}$ , the rearrangement leads to the formation of two substituted phenylimidobenzophenones, part of the substance yielding the phenylimide of the substituted benzophenone, for instance  $(\text{XC}_6\text{H}_4)(\text{C}_6\text{H}_5)\text{C} : \text{NC}_6\text{H}_5$ , part forming a substituted phenylimido derivative of benzophenone itself, namely,  $(\text{C}_6\text{H}_5)_2\text{C} : \text{NC}_6\text{H}_4\text{X}$ .

A study of the proportions in which the groups migrate in a series of such derivatives promises to shed light on a number of interesting questions. In the first place, exactly the same rearrangements have been observed by Stieglitz and Vosburgh<sup>5</sup> in the study of triarylmethylhalogenamines, and, recently, by Stieglitz and Senior<sup>6</sup> in the case of the triarylmethyl azides. In all three series the assumption of the formation of intermediate univalent nitrogen derivatives as the actually rearranging substances gives us, according to Stieglitz, the best explanation of the rearrangements. Then, corresponding compounds in the three series, such as  $(\text{XC}_6\text{H}_4)(\text{C}_6\text{H}_5)_2\text{C.NHOH}$ ,  $(\text{XC}_6\text{H}_4)(\text{C}_6\text{H}_5)_2\text{C.NH}(\text{Hal})$ ,  $(\text{XC}_6\text{H}_4)(\text{C}_6\text{H}_5)_2\text{C.N}(\text{N}_2)$  could well yield the identical rearranging compound  $(\text{XC}_6\text{H}_4)(\text{C}_6\text{H}_5)_2\text{C.N}$ . The conditions for the rearrangement in each of these series vary as to the temperature and other environment factors,

<sup>1</sup> The material presented here forms part of a dissertation in fulfilment of the requirements for the Ph.D. degree (1914).

<sup>2</sup> 8th Intern. Congr. Appl. Chem., **25**, 443 (1912); *Ber.*, **46**, 2147 (1913); *THIS JOURNAL*, **36**, 272 (1914).

<sup>3</sup> Stieglitz and Leech, *THIS JOURNAL*, *loc. cit.*

<sup>4</sup> See the references to the literature, *THIS JOURNAL*, **36**, 272 (1914).

<sup>5</sup> 8th Intern. Congr. Appl. Chem., **25**, 444 (1912) and dissertation work of Isabella Vosburgh, University of Chicago, completed in 1913.

<sup>6</sup> Dissertation work of James K. Senior, University of Chicago, completed in 1914.

but the rearrangement of the univalent nitrogen derivative, being intramolecular, might very well be largely independent of environment. The determinations of the proportions in which the various radicals  $C_6H_5$ ,  $XC_6H_4$ , migrate in the rearrangement of corresponding compounds in each of the three series would give us, therefore, the necessary data for quantitative comparisons of the reactions in the three series.

In the second place, such quantitative determinations would show what differences, if any, are shown in the migration of aryl groups  $XC_6H_4$  with various negative or positive substitution groups in them ( $X = H, Cl, Br, NO_2, CH_3$ , etc.), thus giving a definite answer to the question whether certain groups are more easily lost by carbon and drawn to nitrogen than others. In previous studies of this problem, conclusions have been based, either on the behavior of the groups in question in related but different substances (*e. g.*,  $C_6H_5CONHBr$  and  $NO_2C_6H_4CONHBr$ <sup>1</sup>) or on the behavior of ketoximes, in which stereoisomerism is supposed to play the major role in determining the migration of a given radical. For the triphenylmethane derivatives this complication is eliminated and we have, furthermore, all the groups in question in exactly the same rearranging molecule, *e. g.*,  $(C_6H_5)(XC_6H_4)(YC_6H_4)C.N$  and, therefore, under strictly comparable conditions. The problem is thus reduced to its simplest terms.<sup>2</sup>

Stieglitz and Leech having examined only *p*-chlorophenyldiphenylmethylhydroxylamine in regard to the proportion in which the phenyl and the chlorophenyl groups migrate to the nitrogen, I took up, at the suggestion and under the direction of Professor Stieglitz, the further investigation of this problem at this point. For this purpose the rearrangement of *p*-bromophenyl-diphenylmethylhydroxylamine, of di-*p*-chlorophenyl-phenylmethylhydroxylamine and finally of *p*-chlorophenyl-*p*-bromophenyl-phenylmethylhydroxylamine was studied by me.

The interesting result was obtained that whereas bromophenyl-diphenylmethylhydroxylamine,  $(BrC_6H_4)(C_6H_5)_2CNHOH$ , exactly as the corresponding chloro derivative studied by Leech, rearranges so that, roughly, in two-thirds of the rearranging molecules a phenyl group and in the remaining third the bromophenyl group migrates, the ratio is reversed when one subjects dichlorophenyl-phenylmethylhydroxylamine,  $(ClC_6H_4)_2(C_6H_5)CNHOH$ , to the rearrangement. In this case for two-thirds of the rearranging molecules it is the chlorophenyl group that migrates and in the remaining third the phenyl group. Furthermore,

<sup>1</sup> Hoogewerff and van Dorp, *Rec. trav. chim.*, 6, 373 (1887), etc.

<sup>2</sup> A further question which is being studied is that of the effect of the positions of the substituting groups (ortho, meta and para) on the migration. It is expected to produce experimental evidence concerning the nature of the charges on the carbon atoms holding the aryl groups to the methyl carbon atoms and thus to secure evidence on certain of Fry's assumptions concerning the charges in the benzene derivatives.—J. S.

in the case of chlorophenyl-bromophenyl-phenylmethylhydroxylamine,  $(\text{ClC}_6\text{H}_4)(\text{BrC}_6\text{H}_4)(\text{C}_6\text{H}_5)\text{CNHOH}$ , roughly one-third of the rearranging molecules show a migration of the chlorophenyl group, the bromophenyl group and the phenyl group, respectively. This result certainly would indicate that there is no marked effect of the halogens on the tendency of the aryl group to migrate to the nitrogen.<sup>1</sup>

### Experimental Part.

*p* - Bromophenyldiphenylmethylhydroxylamine,  $(\text{BrC}_6\text{H}_4)(\text{C}_6\text{H}_5)_2\text{CNHOH}$ .—This was prepared according to Gomberg<sup>2</sup> from benzophenone-dichloride and bromobenzene by the Friedel and Craft reaction. The chloride was treated with hydroxylamine by a modification of the methods of Mothwurf<sup>3</sup> and of Stieglitz and Leech.<sup>4</sup> Many futile preliminary attempts by these methods showed that it is necessary to have the hydroxylamine solution very concentrated, for otherwise the principal reaction takes place between the triarylmethylchloride and the alcohol, forming the ether  $(\text{C}_6\text{H}_5)_2(\text{BrC}_6\text{H}_4)\text{COCH}_3$ . Even with this precaution some of the ether was always formed.

A saturated solution of 3.2 g. of hydroxylamine hydrochloride in warm methyl alcohol was added to a solution of sodium methylate (1 g. of sodium dissolved in the least quantity of methyl alcohol). It is desirable not to have any excess of the sodium methylate present and this was carefully determined by evaporation of a drop of the solution on a crucible lid and gentle ignition of any residue. If any alkaline substance remained, more hydroxylamine hydrochloride was added to the methylate solution until the test gave a negative result. The sodium chloride formed in the reaction was removed by filtration and the filtrate evaporated at 20 mm. pressure and 40° to a volume of 10 cc. This treatment gave a very concentrated hydroxylamine solution and but little of the hydroxylamine escaped.<sup>5</sup> The approximate strength of the solution was determined by titration of 0.5 cc. of it with 0.1 *N* hydrochloric acid, methyl orange being used as the indicator.<sup>6</sup>

Three grams of *p*-bromophenyl-diphenylmethyl chloride, dissolved in 30 cc. of anhydrous benzene, were added to the 10 cc. of the alcohol solution of hydroxylamine. After the mixture had stood a few hours the small quantity of hydroxylamine hydrochloride which had separated was removed by filtration and the filtrate evaporated at 20 mm. pressure

<sup>1</sup> The discussion of minor differences in the migration of these radicals and the comparison of the results obtained with corresponding hydroxylamines, chloroamines and azides will be presented in another paper by Professor Stieglitz.

<sup>2</sup> *Ber.*, 37, 1633 (1904).

<sup>3</sup> *Ibid.*, 37, 3152 (1904).

<sup>4</sup> *THIS JOURNAL*, 36, 3152 (1913).

<sup>5</sup> See Lobry de Bruyn, *Rec. trav. chim.*, 10, 100 (1891).

<sup>6</sup> Lobry de Bruyn, *loc. cit.*

and 50°. A yellow, gummy residue, consisting chiefly of the bromophenyl-diphenylmethylhydroxylamine, was left. This base was extracted with dry ether and the extract treated with an excess of dry hydrogen chloride. The salt,  $(\text{BrC}_6\text{H}_4)(\text{C}_6\text{H}_5)_2\text{CNH}_2\text{OHCl}$ , separated at once as a white solid. The salt becomes slightly soluble in ether after a large excess of the acid is introduced. It was collected on a filter, washed several times with ether, and once quickly with cold dilute (about 3 molar) hydrochloric acid to remove hydroxylamine hydrochloride.<sup>1</sup>

From 3 g. of bromophenyl-diphenylmethylchloride, 1.8 g. of the purified salt was obtained. This was analyzed by titration of the hydrochloric acid with silver nitrate solution by the Volhard method.

Subst. 0.1711, 0.1730; cc. 0.1  $N$   $\text{AgNO}_3$ , 4.34, 4.37.

Calc. for  $(\text{BrC}_6\text{H}_4)(\text{C}_6\text{H}_5)_2\text{CNH}_2\text{OHCl}$ :  $\text{HCl}$ , 9.33. Found: 9.25, 9.19.

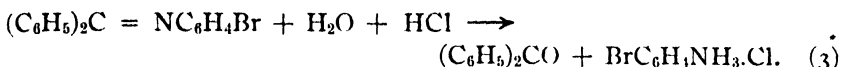
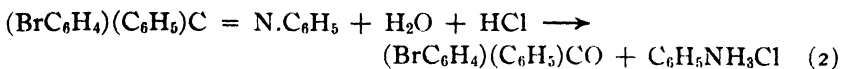
The salt reduces Fehling's solution when boiled, but not in the cold, melts at 144–5° with decomposition, is soluble in alcohol, but not in ligroin and but slightly soluble in ether.

**Rearrangement of *p*-Bromophenyl-diphenylmethylhydroxylamine.**—The free base,  $(\text{BrC}_6\text{H}_4)(\text{C}_6\text{H}_5)_2\text{CNHOH}$ , was obtained from the hydrochloride just described by treatment of the latter with 20% sodium hydroxide solution and extraction of the base with ether. The ether solution was dried with potassium carbonate and the solvent evaporated in a current of dry air. The base thus obtained was a pale yellow viscous liquid or gum. Some of it (1.35 g.) was dissolved in 30 cc. of anhydrous ether and powdered phosphorus pentachloride (2.5 g.) was added to it. When the mixture was allowed to stand at room temperature for a few hours a trace of a yellow deposit collected on the phosphorus chloride. The mixture was then heated on an electric bath for two hours and a greater amount of the yellow deposit collected. The molecular rearrangement was expected to yield the two phenylimidobenzophenones, *p*-bromophenylimidobenzophenone,  $(\text{C}_6\text{H}_5)_2\text{C} : \text{NHC}_6\text{H}_4\text{Br}$  and phenylimidobromobenzophenone,  $(\text{BrC}_6\text{H}_4)(\text{C}_6\text{H}_5)\text{C} : \text{NH.C}_6\text{H}_5$ . To insure that these bases should be present in the form of their salts, some ether (2 cc.) saturated with hydrogen chloride was added to the reaction product. The supernatant liquid was then decanted through a filter from the main residue and the residue was washed with ether containing some hydrogen chloride. Since partial hydrolysis of some of the imidoketones by traces of moisture would form anilines and since aniline hydrochlorides are somewhat soluble in ether containing an excess of hydrogen chloride, it was always possible that some of the aniline, if any were present here, might be dissolved by this treatment. For the recovery of any such substance, the ether filtrate was evaporated almost to dryness, a small amount of

<sup>1</sup> The presence of this salt was indicated by the hydrogen chloride content of the product when it was not purified in this way.



water added to the residue, and this warmed to decompose the phosphorus oxychloride. This aqueous solution and the trace of solid on the filter were then added to the main residue. This was then warmed with alcohol (10 cc.) and dilute hydrochloric acid (5 cc.) for an hour on a steam bath to completely hydrolyze the imidoketones.



The alcohol was removed by evaporation of the solution almost to dryness, followed by a second evaporation after some acidulated water had been added to the residue. Now, water (15 cc.) was added to the product and the solution twice extracted with 15 cc. of ether to remove the ketones. These ketones were identified as described further on. The aqueous solution contained the aniline and bromoaniline hydrochlorides. It was made alkaline, saturated with sodium chloride and the free anilines extracted with two portions of 25 cc. each of ether. The extract was filtered into a weighed beaker and 2 to 3 cc. of ether saturated with hydrogen chloride were added to this filtrate to convert the anilines into hydrochlorides. Because of the partial solubility of these salts in such an acid-ether solution, the ether and the water held in solution by it were evaporated in a current of dry air and the salts remaining were dried *in vacuo*. The dried salts were washed once with 10-15 cc. of absolute ether, dried again, and weighed. The *p*-bromophenyl-diphenylmethylhydroxylamine (1.35 g.) used in the rearrangement yielded 0.2075 g. of aniline hydrochloride and bromoaniline hydrochloride.

Two other quantitative rearrangements of the base were made by this method. In the first a yield of 0.2145 g. of aniline salts was obtained from 1.08 g. of the base and in the second the yield of the salts was 0.2865 g. when 1.17 g. of the base was used. Theoretically 1 g. of the base could yield either 0.36 g. of aniline hydrochloride or 0.58 g. bromoaniline hydrochloride.

These mixtures of aniline and bromoaniline hydrochlorides were analyzed to ascertain the molar ratios of the aniline and bromoaniline. The bromination method of Curme<sup>1</sup> was used.

Subst. 0.0589, 0.0569, 0.0659; cc. 0.1 *N* KBrO<sub>3</sub>, 21.65, 21.31, 24.63. Found: aniline hydrochloride, 74.73, 76.81, 76.58; bromoaniline hydrochloride, 25.27, 23.19, 23.42.

**Identification of Aniline and Bromoaniline.**—The method of separating aniline and chloroaniline used by Stieglitz and Leech<sup>2</sup> proved satisfactory for separating and identifying the aniline and bromoaniline of this re-

<sup>1</sup> THIS JOURNAL, 35, 1162 (1913).

<sup>2</sup> *Loc. cit.*

arrangement. The hydrochlorides were converted into the oxalates and the greater solubility of the aniline oxalate in hot water permitted its separation from the bromoaniline oxalate. The former, in water solution and made alkaline, gave the violet color with bleaching powder solution; and the latter, freed from the acid, gave crystals from ether solution, which melted at  $62^{\circ}$ . These when mixed with pure *p*-bromoaniline,<sup>1</sup> melted at  $62-63^{\circ}$ .

**Identification of Benzophenone and Bromobenzophenone.**—The ether containing the ketones in solution was evaporated. The residue was quickly washed with a small amount of ligroin and then about seven-eighths of the residue was dissolved in warm ligroin (b. p.  $70-80^{\circ}$ ). The small quantity of residue remaining melted at  $81^{\circ}$  (pure *p*-bromobenzophenone melts at  $82.5^{\circ}$ ). The ligroin solution was evaporated to dryness and two-thirds of the residue dissolved. This treatment was repeated until about one-eighth of the original residue was in solution. A few crystals obtained from this solution melted at  $46-47^{\circ}$  and when they were mixed with pure benzophenone they melted at  $47-48^{\circ}$  (pure benzophenone melts at  $48.5^{\circ}$ ).

**Rearrangement of *p*-Bromophenyl-diphenylmethylhydroxylamine Hydrochloride by Means of Phosphorus Pentoxide.**—Bromophenyl-diphenylmethylhydroxylamine hydrochloride (0.8 g.) and phosphorus pentoxide (0.9 g.) were placed together in a test tube and gradually warmed in a metal bath. At  $107^{\circ}$  a rapid reaction took place and the mixture expanded to about three times its original volume into a brown gummy mass. The mass was kept at this temperature for 20 minutes and then cooled.<sup>2</sup> The subsequent treatment was similar to that described above for the product of the rearrangement of the free base. Approximately 0.1 g. of the hydrochlorides of aniline and bromoaniline was obtained. The aniline gave the characteristic test with bleaching powder solution. No further attempts at effecting rearrangements by means of phosphorus oxide were made as the pentachloride seemed to give more satisfactory yields.

**Di-*p*-chlorophenyl-phenylmethylhydroxylamine,  $(\text{ClC}_6\text{H}_4)_2(\text{C}_6\text{H}_5)\text{-CNHOH}$ .**—This was made by Gomberg's method<sup>3</sup> from dichlorobenzophenone by the Grignard reaction. The reagent was used according to the proportions given by Houben,<sup>4</sup> *i. e.*, 2.36 g. of special magnesium, 17.5 g. of bromobenzene, and 120 cc. of ether. After a few hours, when the reaction between the magnesium and the bromobenzene was com-

<sup>1</sup> Kahlbaum's pure bromoaniline, melting at  $63-64^{\circ}$ .

<sup>2</sup> The reaction seems to take place slowly even when the mixture is heated only slightly, as shown by the fact that the yellow tint of the mixture grew deeper in color when it was pressed hard against the sides of the test tube with a glass rod.

<sup>3</sup> *Ber.*, 39, 3279 (1906).

<sup>4</sup> *Ibid.*, 36, 3087 (1903).

plete, 9 g. of the solid di-*p*-chlorobenzophenone were added. This ketone is only moderately soluble in ether but it dissolved at once in the Grignard reagent. The solution must be kept free from moisture. It was warmed for three hours on a water bath and the magnesium compound was then decomposed with water. The excess of bromobenzene used in making the Grignard reagent and the benzene formed from it later were removed by steam distillation and the light colored insoluble gum remaining in the water was washed free from magnesium hydroxide with dilute hydrochloric acid. The gum was dissolved in ligroin and dried with fused calcium chloride. The solution was filtered and the solvent evaporated spontaneously in a desiccator over paraffin shavings. In three hours crystals of the carbinol began to form and 8.6 g. of the carbinol had separated out overnight. The carbinol melted at  $85^{\circ}$  without recrystallization. Gomberg did not succeed in obtaining this carbinol crystallized until he had taken it through a long troublesome method of purification. The preparation was twice repeated and the crystallization similarly obtained. The carbinol was converted into the chloride,  $(\text{ClC}_6\text{H}_4)_2(\text{C}_6\text{H}_5)\text{CCl}$ , in the usual manner by dry hydrogen chloride passed into a carbon disulfide solution of the carbinol. The chloride thus formed was a gum at first and assayed 94% of the calculated amount of chlorine when it was hydrolyzed in alcohol solution with excess of alkali. This gum was used for the preparation of the hydroxylamine, but about 5 g. of it were left in a desiccator over solid potassium hydroxide and in a month's time crystals had formed on the sides of the beaker. These were pushed down into the gum and in several days the whole had become solid. This impure solid melted at  $43\text{--}50^{\circ}$ .

Subst. 0.4333 g.; cc. 0.1 *N* KOH 11.58. Calc. for  $(\text{ClC}_6\text{H}_4)_2(\text{C}_6\text{H}_5)\text{CCl}$ : Cl, 10.21. Found: 9.50.

Gomberg was not successful in getting this gum to solidify. The solidification is slow and time did not permit further efforts at the purification of the product. The chloride, as a gum, was allowed to act on a strong solution of hydroxylamine, in the way described above for bromophenyl-diphenylmethylchloride. The free base remaining after the alcohol and benzene were removed, was extracted with ether and hydrogen chloride added to the ether extract. The hydrochloride,  $(\text{ClC}_6\text{H}_4)_2(\text{C}_6\text{H}_5)\text{CNH}_2\text{OHCl}$ , separated at once as a white solid. The salt was removed by filtration and washed well with ether and once quickly washed with cold dilute hydrochloric acid. It is slightly soluble in ether, soluble in alcohol, but insoluble in ligroin and benzene. It reduces boiling Fehling's solution, and melts at  $129\text{--}30^{\circ}$  into a pale yellow liquid which soon reddens when left at that temperature.

Subst. 0.2287, 0.2869; cc. 0.1 *N*  $\text{AgNO}_3$ , 5.85, 7.29.  
Calc. for  $(\text{ClC}_6\text{H}_4)_2(\text{C}_6\text{H}_5)\text{CNH}_2\text{OHCl}$ : HCl, 9.58. Found: 9.32, 9.26.

**Rearrangement of Di-*p*-chlorophenyl-phenylmethylhydroxylamine.**—

The free base was obtained from the hydrochloride described above by treatment of the salt with 20% alkali solution and extraction with ether. The ether solution was dried over potassium carbonate and the ether evaporated. The base was left as a pale yellow, syrupy liquid or gum which is soluble in ether, alcohol, ligroin, and benzene. The substance (1.47 g.) was dissolved in ether (30-40 cc.) and phosphorus pentachloride (2.5 g.) was added to the solution. The subsequent treatment was similar to that of the bromophenyl-diphenylmethylhydroxylamine as given above.

A yield of 0.4229 g. of mixed aniline hydrochlorides was obtained from 1.47 g. of the base. A second rearrangement of 1.21 g. of the base gave 0.354 g. of the aniline salts.

A complete rearrangement would yield at most 0.37 g. of aniline hydrochloride, or 0.47 g. of chloroaniline hydrochloride per gram of substance.

A quantitative analysis of the aniline salts obtained from each of the rearrangements was made by the bromination method for their molar ratios.

Subst. 0.0794, 0.0767; cc. 0.1 *N* KBrO<sub>3</sub>, 25.13, 23.93.

Found: aniline hydrochloride, 38.41, 36.30; chloroaniline hydrochloride, 61.56, 63.70.

**Identification of the Anilines.**—A qualitative separation of the two anilines was made by the method of Stieglitz and Leech.<sup>1</sup> When separated, the aniline gave the violet color test with bleaching powder and the chloroaniline gave crystals which melted at 68-69°, and when they were mixed with pure chloroaniline they melted at 68-69° (pure chloroaniline melts at 69°).

**Identification of Chlorobenzophenone and Dichlorobenzophenone.**—

The ether was evaporated from the *p*-chlorobenzophenone and di-*p*-chlorobenzophenone solution, leaving a large bulk of flaky crystals. Preliminary tests with a mixture of known mono- and di-chlorobenzophenones showed that the latter is the less soluble in ligroin and that the two could be separated by virtue of this difference. The ketones obtained from the rearrangement were dissolved in a small quantity of warm ligroin. When a few crystals had separated from the solution, as it cooled, they were collected in a filter. They melted at 139° and when they were mixed with pure *p*-dichlorobenzophenone they melted at 141-142° (pure *p*-dichlorobenzophenone melts at 143°). The filtrate still containing the greater portion of the ketones, was evaporated to dryness and three-quarters of the residue again dissolved in ligroin. This process was repeated until the last extraction contained about one-eighth of the original ketone residue. About one-half of this was crystallized from the solution and the melting point of these crystals determined. They melted at 79-

<sup>1</sup> *Loc. cit.*, p. 296.

80°, and when they were mixed with pure *p*-chlorobenzophenone<sup>1</sup> they melted at 78–80°.

**Di-*p*-bromophenyl-phenylmethylhydroxylamine Hydrochloride**,  $(\text{BrC}_6\text{H}_4)_2(\text{C}_6\text{H}_5)\text{C.NH}_2\text{OH.Cl}$ . — Di-*p*-bromophenyl-phenylmethylchloride was prepared by Gomberg's method.<sup>2</sup> The corresponding carbinol,  $(\text{BrC}_6\text{H}_4)_2(\text{C}_6\text{H}_5)\text{COH}$ , which was first obtained, melted at 113.5° when recrystallized from ligroin. It melted at the same temperature when twice recrystallized. Gomberg gives the melting point as 110°. The chloride,  $(\text{BrC}_6\text{H}_4)_2(\text{C}_6\text{H}_5)\text{CCl}$ , was dissolved in benzene and added to a solution of hydroxylamine in alcohol. The molecular proportions of substances, and the method of procedure used in the previous preparations were repeated here. The alcohol and benzene were removed by distillation under diminished pressure and without the temperature rising above 60°. A gummy residue remained and consisted principally of the free base dibromophenyl-phenylmethylhydroxylamine. This base was extracted with ether and hydrogen chloride introduced into the solution. A small quantity of white precipitate separated out at first but it redissolved as the solution became more strongly acid. The acid and ether were now evaporated and a mobile liquid was left. Low boiling ligroin (b. p. 40–60°) was added to it and the mixture stirred. The liquid, which was but little soluble in the ligroin, began to solidify immediately. The di-*p*-bromophenyl-phenylmethylhydroxylamine hydrochloride thus formed is as soluble in methyl and ethyl alcohol and ether as is the dibromophenyl-phenylmethylchloride itself, but it is not soluble in ligroin, while the latter is. The salt was washed well with ligroin (b. p. 70–80°) and once with cold dilute hydrochloric acid. It reduces boiling Fehling's solution and softens at about 75°.

Subst. 0.2850, 0.3113; cc. 0.1 *N* AgNO<sub>3</sub>, 5.73, 6.31.

Calc. for  $(\text{BrC}_6\text{H}_4)_2(\text{C}_6\text{H}_5)\text{CNH}_2\text{OHCl} \cdot \text{HCl}$ , 7.73. Found: 7.34, 7.40.

**Rearrangement of Di-*p*-bromophenyl-phenylmethylhydroxylamine.** — The free base,  $(\text{BrC}_6\text{H}_4)_2(\text{C}_6\text{H}_5)\text{CNHOH}$ , was prepared from the hydrochloride in the usual way. It was obtained as a yellow viscous liquid. Some of the base (1.6 g.) was dissolved in 30 cc. of ether and 3 g. of phosphorus pentachloride added to the solution. The mixture was warmed at the boiling point of the ether for two hours. The imido-benzophenones appeared in that time as indicated by the yellow color of the mixture. The mixture was then subjected to hydrolysis and to the isolation of the ketones and the aniline hydrochlorides. The yield of the mixed aniline and bromoaniline hydrochlorides from the base (1.6 g.) was 0.4785 g. A second rearrangement of 1.11 g. base gave 0.3104 g. of mixed aniline salts. Theoretically one gram of base could give 0.30 g. aniline hydro-

<sup>1</sup> Kahlbaum's *p*-chlorobenzophenone melted at 77–78°.

<sup>2</sup> *Ber.*, 39, 3280 (1906).

chloride or 0.48 g. of bromoaniline hydrochloride. Each quantity of the mixed aniline hydrochloride was analyzed for the molar ratios of the anilines by the bromination method.

Subst. 0.0513, 0.0439; cc. 0.1 *N* KBrO<sub>3</sub>, 12.80, 11.04.

Found: aniline hydrochloride, 30.25, 31.05; bromoaniline hydrochloride, 69.76, 68.95.

**Identification of Aniline and Bromoaniline.**—The aniline and bromoaniline were separated exactly as were the bases from the rearranged *p*-bromophenyl-diphenylmethylhydroxylamine. The aniline oxalate, after separation from the bromoaniline salt, was made alkaline and tested with bleaching powder solution. The violet color confirmed the identity of the aniline. The less soluble bromoaniline oxalate was freed from the oxalic acid and crystallized from ether. The crystals melted at 62–63°, and, when they were mixed with pure bromoaniline, they melted at 63–64° (pure bromoaniline melts at 64°).

**Identification of Bromobenzophenone and Dibromobenzophenone.**—The ether solution of the ketones was evaporated to dryness in a current of air. Of the *p*-bromobenzophenone and *p*-dibromobenzophenone, the latter is the less soluble in ligroin (b. p. 70–80°) and by fractional crystallization from that solvent some of it was isolated. It melted at 167° and when it was mixed with synthetic dibromobenzophenone it melted at 167–168° (pure dibromobenzophenone melts at 172–173°). The ligroin solution containing the more soluble portion of the ketones was evaporated to dryness and the process for separating monochlorobenzophenone from dichlorobenzophenone was followed. The crystals thus isolated melted at 78–80° (pure *p*-bromobenzophenone melts at 82.5°).

***p*-Chlorophenyl-*p*-bromophenyl-phenylcarbinol**, (ClC<sub>6</sub>H<sub>4</sub>)(BrC<sub>6</sub>H<sub>4</sub>)-(C<sub>6</sub>H<sub>5</sub>)COH.—This carbinol and the corresponding chloride required for the next experiment are not described in the literature and probably have not been made. For the preparation of the carbinol, *p*-chlorobenzophenone was first obtained from benzoylchloride and chlorobenzene with the aid of the Friedel and Crafts reaction.<sup>1</sup> The chlorobenzophenone was converted into the dichloride by treatment with phosphorus pentachloride by the method used by Kekulé and Franchmont in converting benzophenone into benzophenone dichloride.<sup>2</sup> The dichloride was fractionally distilled.<sup>3</sup> Then, one molar proportion of the *p*-chlorobenzophenonedichloride and two to three of bromobenzene were placed on a steam bath in a round bottom flask with a reflux condenser attached, and to this solution 1.4 molar proportions of aluminum chloride were gradually added in portions of 5 to 10 g. After

<sup>1</sup> Gomberg, *B. r.*, 39, 3278 (1906).

<sup>2</sup> Mackenzie, *J. Chem. Soc.*, 69, 987 (1896).

<sup>3</sup> Overton, *Ber.*, 26, 28 (1893); Peterson, *Am. Chem. J.*, 46, 332 (1911).

all of the aluminum chloride had been added the mixture was heated two hours longer. It was then cooled and poured on ice and water to decompose the aluminum compound. The excess of bromobenzene was removed by steam distillation and the residue, a dark gum insoluble in water, was well washed with dilute hydrochloric acid to remove the aluminum hydroxide. The gummy residue was extracted with carbon disulfide, the carbon disulfide solution filtered, the filtrate dried over fused calcium chloride, and the solvent evaporated. The dark colored gum remaining was dissolved in warm ligroin (b. p. 70–80°) and the solution left in a cold place overnight. The carbinol separated out in light colored crystals. Recrystallization was twice repeated and the carbinol then melted at 91–93°.

0.2161 g. of the carbinol gave 0.4850 g. CO<sub>2</sub> and 0.0760 g. H<sub>2</sub>O.

Calc. for C<sub>19</sub>H<sub>14</sub>OCIBr: C, 61.03%; H, 3.77%. Found: C, 61.22%; H, 3.93%.

***p*-Chlorophenyl - *p*-bromophenyl - phenylmethylchloride**, (ClC<sub>6</sub>H<sub>4</sub>)-(BrC<sub>6</sub>H<sub>4</sub>)(C<sub>6</sub>H<sub>5</sub>)CCl.—The carbinol was converted into the chloride, (ClC<sub>6</sub>H<sub>4</sub>)(BrC<sub>6</sub>H<sub>4</sub>)(C<sub>6</sub>H<sub>5</sub>)CCl, by a stream of hydrogen chloride passed into a carbon disulfide solution of the carbinol. After the acid was added, the disulfide solution was dried over fused calcium chloride and filtered and the excess of acid and the carbon disulfide evaporated *in vacuo*. The chloride was left as a very viscous liquid. When it was hydrolyzed with excess of 0.1 *N* KOH and the excess of alkali was titrated with 0.1 *N* HCl, it showed 93% of the calculated amount of chlorine. Attempts to crystallize the chloride were, at first, unsuccessful and for this reason the liquid chloride was used in making the hydroxylamine preparation. Later, however, the chloride crystallized from low boiling ligroin. The solid was twice recrystallized from higher boiling ligroin by inoculation of the solution with the crystals first obtained. It now melted at 69–72°.

Subst. 0.2229; cc. 0.1 *N* KOH, 5.44. Calc. for (C<sub>19</sub>H<sub>13</sub>ClBr)Cl: 9.05% Cl (hydrolyzable). Found: 8.67%.

***p*-Chlorophenyl-*p*-bromophenyl-phenylmethylhydroxylamine Hydrochloride**, (ClC<sub>6</sub>H<sub>4</sub>)(BrC<sub>6</sub>H<sub>4</sub>)(C<sub>6</sub>H<sub>5</sub>)CNH<sub>2</sub>OHCl.—The chlorophenyl-bromophenyl-phenylmethylchloride (7 g.) was dissolved in benzene (200 g.) and condensed with a saturated alcoholic solution of hydroxylamine. The solvents were removed by evaporation. The gummy residue remaining was extracted with ether and the ether solution made strongly acid with hydrogen chloride. The hydrogen chloride salt of the hydroxylamine derivation does not precipitate out from the ether solution. After the ether and excess acid were evaporated the triarylmethylhydroxylamine hydrochloride remained as a syrupy liquid; it was treated with low boiling ligroin and the mixture stirred with a glass rod. The salt began to solidify immediately. It is insoluble in ligroin and was purified by being washed well with that solvent. It cannot be washed with dilute

hydrochloric acid as it forms a soft, sticky mass as soon as brought into contact with the water. It is soluble in alcohol, ether, and chloroform. It reduces boiling Fehling's solution and softens at  $45^{\circ}$ , but has no true melting point.

Subst. 0.4155; cc. 0.1 *N* AgNO<sub>3</sub>, 9.41. Calc. for (C<sub>19</sub>H<sub>16</sub>NOCIBr)HCl: Cl, 8.58%. Found: 8.27.

A yield of 5 g. of this salt was obtained from the chloride (7 g.) used.

**Rearrangement of *p*-Chlorophenyl-*p*-bromophenyl-phenylmethylhydroxylamine.** The free base of the salt just described was obtained as a yellow syrupy substance, which under low pressure began to expand as a kind of foam and to spread throughout the beaker as a viscous gum. This behavior is characteristic of all these bases.

Some of the base (2.37 g.) was dissolved in 30-40 cc. of ether and phosphorus pentachloride (4 g.) added to the solution. In twelve hours a slight change in color to yellow indicated a slow formation of the imido ketones at room temperature. The mixture was then heated for two hours at the temperature of boiling ether to complete the rearrangement. The mixture was next subjected to hydrolysis of the imido ketones,<sup>1</sup> and the isolation of the benzophenones and the anilines carried out in the manner described for the previous rearrangements.

The yield of the mixed aniline, chloroaniline and bromoaniline hydrochlorides from the 2.37 g. of base was 0.626 g. In a second rearrangement of 1 g. of base 0.1595 g. of the aniline salts was obtained. A complete rearrangement would give 0.33 g. of aniline hydrochloride, or 0.42 g. of chloroaniline hydrochloride or 0.54 g. of bromoaniline hydrochloride per gram of substance.

A trace of the aniline mixture was made alkaline and treated with bleaching powder solution. A violet color was produced, proving the presence of the unsubstituted aniline. Another part of the aniline mixture was freed from hydrogen chloride and precipitated from ether solution with oxalic acid. The precipitate showed the presence of halogen when heated in a bunsen flame with copper oxide and also when fused with sodium and tested with silver nitrate solution.

The mixed aniline hydrochlorides obtained from each of the rearrangements were analyzed volumetrically for the determination of the molar ratios of the three salts: the hydrochlorides of aniline, chloroaniline and bromoaniline. The bromination and the Volhard methods were used jointly to give sufficient data for the calculations.<sup>2</sup>

<sup>1</sup> Three imido ketones were present, (ClC<sub>6</sub>H<sub>4</sub>)(BrC<sub>6</sub>H<sub>4</sub>)C = N(C<sub>6</sub>H<sub>5</sub>), (ClC<sub>6</sub>H<sub>4</sub>)(C<sub>6</sub>H<sub>5</sub>)C = NC<sub>6</sub>H<sub>4</sub>Br, and (BrC<sub>6</sub>H<sub>4</sub>)(C<sub>6</sub>H<sub>5</sub>)C = NC<sub>6</sub>H<sub>4</sub>Cl.

<sup>2</sup> The reliability of this method of analysis was determined with a known mixture of the three hydrochlorides. For the Volhard method a larger quantity of the mixed salts was used than for the bromination method, as the data show. The method is reliable only to within 5%.



0.0754 g. of the mixed hydrochlorides required 21.68 cc. of 0.1 *N* KBrO<sub>3</sub>; and 0.2128 g. required 12.85 cc. 0.1 *N* AgNO<sub>3</sub>. Found: aniline hydrochloride, 38.0; chloroaniline hydrochloride, 28.8; and bromoaniline hydrochloride, 33.2.

0.0318 g. of the mixed hydrochlorides required 9.24 cc. of 0.1 *N* KBrO<sub>3</sub>, and 0.1276 g. of the same mixture required 7.85 cc. of 0.1 *N* AgNO<sub>3</sub>. Found: aniline hydrochloride, 36.2; chloroaniline hydrochloride, 38.9; and bromoaniline hydrochloride, 24.9.

I wish to express my indebtedness to Professor Stieglitz, not only for the constant interest that he has shown in this investigation and the many helpful suggestions, but also for the encouragement and his kindness toward me personally.

CHICAGO, ILL.

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

## THE MOLECULAR REARRANGEMENT OF TRIPHENYLMETHYLHALOGENAMINES.<sup>1</sup>

BY ISABELLA VOSBURGH.<sup>2</sup>

Received August 1, 1916.

The characteristic Hofmann rearrangement<sup>3</sup> of acid halogen amides, RCONH(Hal), to derivatives of amines RNH<sub>2</sub> forms the basis of the well-known general method of preparation of amines.<sup>1</sup> The rearrangement<sup>5</sup> is analogous in many important respects to the "Beckmann" rearrangement of oximes.<sup>6</sup> When it was found in this laboratory by Stieglitz and Reddick<sup>7</sup> that triphenylmethylhydroxylamine undergoes a rearrangement quite as smoothly as any oxime, Professor Stieglitz proposed to me that I undertake under his direction a parallel investigation on the possibility of effecting rearrangements of the triphenylmethylhalogenamines, Ar<sub>3</sub>CNH(Hal). The investigation of these particularly simple halogen amine derivatives promised to shed light on a number of questions connected with the rearrangements: of those taken up in this in-

<sup>1</sup> See a preliminary report (abstract) by Stieglitz and Vosburgh, *8th Intern. Congr. Appl. Chem.*, **25**, 445 (1912); *Ber.*, **46**, 2151 (1913).

<sup>2</sup> The work reported on in this paper formed the basis of a dissertation submitted to the University of Chicago in part fulfillment of the requirements for the Ph.D. degree. Before Miss Vosburgh could come up for her final examinations, she was the victim of a fatal automobile accident, Dec. 4, 1914, near Mt. Holyoke, Mass. The present posthumous report, except for editing, is in the form in which it was written by Miss Vosburgh.—J. STIEGLITZ.

<sup>3</sup> A. W. Hofmann, *Ber.*, **14**, 2725 (1882); **15**, 408 (1883), etc.

<sup>4</sup> Hofmann, *loc. cit.*; Hoogewerff and van Dorp, *Rec. trav. chim.*, **6**, 373 (1887); **8**, 173 (1889), etc.; Lengfeld and Stieglitz, *Am. Chem. J.*, **15**, 215, 504 (1893); Elizabeth Jeffreys, *Ber.*, **30**, 898 (1897); *Am. Chem. J.*, **22**, 14 (1899).

<sup>5</sup> The analogy was pointed out by Hoogewerff and van Dorp, *loc. cit.*; and by Stieglitz, *Am. Chem. J.*, **18**, 751 (1896).

<sup>6</sup> Beckmann, *Ber.*, **19**, 988 (1886), etc.

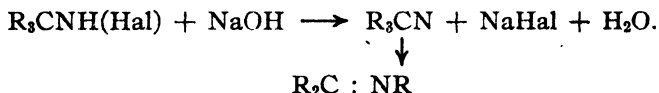
<sup>7</sup> See Stieglitz, Reddick and Leech, *8th Intern. Congr. Appl. Chem.*, **25**, 444 (1912).

vestigation, we have, first, that it promised to lend itself to a further study of the extent to which Stieglitz's theory<sup>1</sup> of the related "Hofmann-Beckmann-Lossen<sup>2</sup>-Curtius<sup>3</sup> rearrangements would hold in the new group of rearrangements, if such should indeed be found to occur. In the second place, it would contribute to a knowledge of the nature of the metal salts that are the active components in the Hofmann rearrangement of acid halogen amides, in which the question of the nature of the salts involved is complicated by the formation of tautomeric salts.

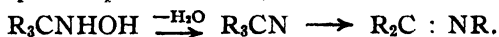
The results obtained have brought definite information concerning both of the questions outlined. The Stieglitz theory<sup>4</sup> of these rearrangements ascribes the rearrangements to the intermediate formation of univalent nitrogen derivatives (*e. g.*,  $\text{RCO.N}$  from  $\text{RCO.NH(Hal)}$ ) which are considered to be the real rearranging substances.<sup>5</sup> The alkyl or aryl group  $\text{R}$  is subsequently torn from the carbon atom by virtue of the powerful unsaturated affinities of the univalent nitrogen atom. We have, for instance,  $\text{RCO.N} \longrightarrow \text{CO} : \text{NR}$ .

The reagents selected to effect the rearrangement of the various classes of compounds are just those which one would anticipate would be necessary to facilitate the formation of the univalent nitrogen derivative from the original material.

In agreement with these considerations we have found that triphenylmethylhalogenamines readily undergo the same kind of rearrangement under the influence of *bases*.



It is of interest to note how, once again, the relation of the reagent to the compound that is to be rearranged is shown and to compare this action with the rearrangement of triphenylmethylhydroxylamine under the influence of phosphorus pentachloride,<sup>6</sup>



It has been found, further, that triarylmethyldichloroamines, like the acid azides  $\text{RCO.N(N}_2\text{)}$ , require simply heat to undergo the rearrange-

<sup>1</sup> *Am. Chem. J.*, **18**, 751 (1896); **29**, 49 (1901).

<sup>2</sup> *Ann.*, **161**, 359 (1872), etc.; L. W. Jones, *Am. Chem. J.*, **48**, 1 (1912).

<sup>3</sup> *Ber.*, **27**, 778 (1895); *J. prakt. Chem.*, **50**, 289 (1894), etc.

<sup>4</sup> The theory is given in detail in *Am. Chem. J.*, **29**, 49 (1901), and only one or two of its most salient features need be considered here.

<sup>5</sup> The theoretical possibility of a direct exchange of  $\text{R}$  for the halogen atom in certain cases is not excluded by the theory, which emphasizes simply that the path over the univalent nitrogen derivatives seems to be the easiest and the ordinary one and possibly in the majority of cases the only path. See Stieglitz and Leech, *Ber.*, **46**, 2147 (1913) and Stieglitz and Leech, *THIS JOURNAL*, **36**, 272 (1914).

<sup>6</sup> Stieglitz, Reddick and Leech, *loc. cit.*

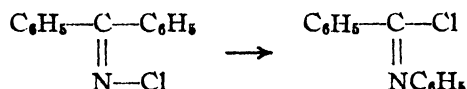
ment, chlorine being given off and the rearrangement taking place with explosive violence at 120–130°.



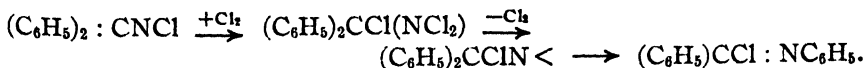
Again, we have found that alkylated triarylchloroamines, *e. g.*,  $R_3CN(CH_3)Cl$ , in which the formation of univalent nitrogen would be very greatly obstructed, or altogether prevented, do not undergo the rearrangement<sup>1</sup> when treated exactly in the same way as the halogen amines,  $R_3CNH(Hal)$  or as the dihalogen amines,  $R_3CNCl_2$ .

All of these results, therefore, show that the above theory of the rearrangements is borne out by the behavior of triarylmethylhalogenamines, as thus far observed.

Closely related to these questions is the following: all attempts to effect a rearrangement of chloroimidobenzophenone,  $(C_6H_5)_2C : NCl$ , by the action of heat, or of alkalis, under various conditions have proved unsuccessful,<sup>2</sup> although this is the very compound which one should expect to be readily rearranged, if the rearrangements involve simply direct exchanges of radicals, as is assumed by Beckmann and some other prominent chemists.<sup>3</sup>



This is in interesting contrast to the ready rearrangement of the closely related triphenylmethylbromoamine,  $(C_6H_5)_3CNHBr$ , the essential difference between the two compounds being that the latter by the loss of hydrogen bromide can give a univalent nitrogen derivative, the former cannot; the chloroimide corresponds in that respect essentially to  $(C_6H_5)_3CN(CH_3)Cl$ , which also does not rearrange, as has been stated above. Now, the behavior of triphenylmethyldichloroamine,  $(C_6H_5)_3CNCl_2$ , in rearranging under the influence of heat suggested<sup>4</sup> that the action of chlorine on the chloroimide might lead to the formation of an intermediate addition product which would correspond in structure to triphenylmethyldichloroamine and which might lose chlorine from the nitrogen and then rearrange.



<sup>1</sup> Stieglitz and Leech (THIS JOURNAL, 36, 272 (1914)) have recently made the important observation that the analogous  $(C_6H_5)_3CN(CH_3)OH$  is rearranged to a methylaniline derivative.

<sup>2</sup> Unpublished work of Stieglitz and Parke H. Watkins.

<sup>3</sup> Beckmann, *Ber.*, 19, 988 (1886); 27, 300 (1894); Hoogewerf and van Dorp, *Rec. trav. chim.*, 8, 173 (1889); Hantzsch, *Ber.*, 24, 3516 (1891); Kuhara, *Mem. Coll. Sci. Eng. Kyoto*, 1, 254 (1903–1908); 2, 387 (1909–1910); 6, 1 (1913).

<sup>4</sup> Stieglitz and Leech, *Ber.*, 46, 2147 (1913).

Under the conditions tried by us, namely, the action of chlorine at  $120^{\circ}$  to  $150^{\circ}$ , no rearrangement of this nature was, however, observed. Possibly at that high temperature no measurable absorption of chlorine by the  $\text{—C:N—}$  group takes place.

Concerning the second question raised in connection with this investigation (see above), the relations, briefly are as follows: the rearrangement of acid halogen amides is effected by bases, (alkalies,<sup>1</sup> calcium oxide,<sup>1</sup> silver carbonate,<sup>1</sup> alkali alcoholates,<sup>2</sup> etc.) and there is no doubt that the active substances leading presumably primarily to the formation of acylimides,  $\text{RCO.N}$ , as just now discussed, are the metal salts of the acid halogen amides. Now, these salts may have either of two structures—they may be nitrogen salts,  $\text{RCO.NMe(Hal)}$  or oxygen salts,  $\text{RC(OMe)N.Hal}$ . The first structure was assumed for them by their discoverer, Hofmann,<sup>3</sup> by Hoogewerff and van Dorp,<sup>3</sup> Lengfeld and Stieglitz<sup>3</sup> and others of the early workers in this field. The second structure was suggested for them by Hantzsch<sup>4</sup> as the result of his study of acid chloroamides as tautomeric compounds, and by Stieglitz, in some later work, on the basis of the formation of oxygen ethers by the methylation of the acylchloroamides with diazomethane.<sup>5</sup> As a result of the investigations of Ley,<sup>6</sup> Hantzsch,<sup>7</sup> Baly, Marsden and Stewart,<sup>8</sup> and Acree<sup>9</sup> on tautomeric salts, it seems now reasonably certain that we have both salts present together in solution in a condition of equilibrium. It is, therefore, uncertain which form of salt, nitrogen salt,<sup>10</sup> or oxygen salt, is directly involved in the rearrangement. In our present investigation the rearrangement of triarylmethylhalogenamines is also effected by bases and there is again no question as to the action being due to the formation of salts, which favor the subsequent reactions that lead to the rearrangements more than do the hydrogen derivatives. In the present instance, these salts can only have the structure  $\text{R}_3\text{CNMe(Hal)}$ , that is, they must be nitrogen salts. This result makes it quite probable that the active components in the rearrangement of the salts of acid halogen amides is also the nitrogen salt,  $\text{RCO.NMe(Hal)}$ , in spite of the fact that it is most likely present in considerably smaller proportions than the oxygen salt, the equilibrium favoring the oxygen salt, according to the work of Hantzsch.

<sup>1</sup> Hofmann, *loc. cit.*

<sup>2</sup> Lengfeld and Stieglitz, *loc. cit.*

<sup>3</sup> *Loc. cit.*

<sup>4</sup> *Ber.*, **35**, 228 (1902).

<sup>5</sup> Stieglitz and Ransom, *Ber.*, **31**, 1055 (1898); *Am. Chem. J.*, **23**, 1 (1900).

<sup>6</sup> *Ber.*, **32**, 1357 (1899); **38**, 973 (1905), etc.

<sup>7</sup> Ley and Hantzsch, *Ber.*, **39**, 3149 (1906).

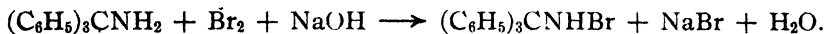
<sup>8</sup> *J. Chem. Soc.*, **89**, 966 (1906).

<sup>9</sup> *Am. Chem. J.*, **37**, 71 (1906), etc.

<sup>10</sup> Schroede, *Ber.*, **42**, 2336 (1909) favored this view.

### Experimental Part.

**Triphenylmethylbromoamine**,  $(C_6H_5)_3CNHBr$ .—The first halogen derivative of a triarylmethylamine prepared was triphenylmethylbromoamine. Hemilian and Silberstein<sup>1</sup> had previously studied the effect of halogens upon triphenylmethylenamines and had concluded that compounds containing from two to seven atoms of the halogen resulted. They gave the formula  $(C_6H_5)_3CNH_2Br_2$  to the bromine derivative. For the present investigation triphenylmethylchloride, obtained by the Friedel and Crafts<sup>2</sup> method, was converted into the amine hydrochloride by the Elbs method, with the modification that ammonia was passed repeatedly into the benzene solution of the chloride in order to obtain a satisfactory yield. The free base was obtained from the hydrochloride by precipitation by ammonium hydroxide in aqueous solution, and was brominated by treatment with bromine and aqueous sodium hydroxide,



The preparation is not an easy one and the observation of the following details will be found useful: Bromine (1.39 g.), weighed in a small bulb with capillary, was added to the dry amine (2.1 g.). The mixture, placed in an ice and salt preparation, was treated with a few drops of chloroform and a 10% solution of sodium hydroxide (3.25 cc.). The mixture was shaken for fifteen minutes, then more chloroform was added to it, and the two layers separated by means of a separatory funnel. The chloroform solution was dried a few minutes with calcium chloride and the chloroform then immediately evaporated in a blast of air. A yellow gum remained, part of which dissolved on the addition of ligroin (b. p. 70–80°). The evaporation of the ligroin in the cold gave a yellowish substance, which is likely to remain semi-solid. In one case, however, a few large crystals were obtained, and, thereafter, inoculation made the preparation of a crystalline product comparatively simple. By repeated recrystallizations from ligroin, a compound melting at 63° was obtained. The triphenylmethylbromoamine thus prepared, was analyzed by titration of the iodine liberated according to the equation



Subst., 0.0746; cc. 0.1 N  $Na_2S_2O_3$ , 4.39.

Calc. for  $C_{19}H_{15}NBr$ : Br, 23.64%. Found: 23.57.

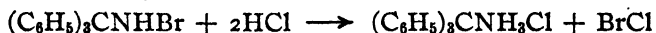
The structure of triphenylmethylbromoamine was confirmed as follows:<sup>3</sup> Treatment of the bromoamine with dry hydrogen chloride gas in ether solution precipitated triphenylmethylamine hydrochloride. This was identified by its melting point (244°), and by its conversion into the

<sup>1</sup> *Ber.*, 17, 748 (1884).

<sup>2</sup> *Ibid.*, 33, 3147 (1900).

<sup>3</sup> See Stieglitz and Earle, *Am. Chem. J.*, 30, 399, 412 (1903); Hilpert, *Ibid.*, 40, 155 (1908); Peterson, *Ibid.*, 46, 325 (1911).

free base, which melted at  $102^{\circ}$ , when heated by itself or mixed with synthetic triphenylmethylamine, we have:



**The Rearrangement of Triphenylmethylbromoamine.**—*1. By Treatment with Soda-lime.* Preliminary experiments showed that when the bromoamine is heated with soda-lime over a flame, a sudden action occurs with the evolution of brown fumes and the formation of a bright yellow substance. From this mass the yellow substance phenylimidobenzophenone may be extracted and identified by hydrolysis, the aniline formed being readily recognized by the chloride of lime test. Occasionally, however, this method gave negative results, probably because the mixture of bromoamine and soda-lime had not been heated sufficiently high.

The following method gives uniformly good results: Half a gram of the bromoamine is mixed with a gram of finely powdered soda-lime and the mixture is heated in a hard glass test tube by immersion in a metal-bath kept at  $110$ – $120^{\circ}$ . As soon as the intense yellow product is formed, a small part of the mixture is tested by being boiled with an excess of hydrochloric acid, the resulting solution being neutralized and tested with calcium hypochlorite. If a strong aniline reaction is shown, the remainder of the mass is extracted with benzene. The evaporation of the solvent leaves crude phenylimido-benzophenone, melting at  $89^{\circ}$ . Recrystallized from absolute alcohol, it formed yellow crystals which softened a little at  $106^{\circ}$  but melted at  $110^{\circ}$ . A synthetic preparation,<sup>1</sup> obtained from aniline and benzophenonedichloride, gave a melting point of  $111$ – $112^{\circ}$ . A mixture of this preparation with the product obtained by the rearrangement of the bromoamine melted at  $111^{\circ}$ . Their identity is thus established.

In confirmation of the structure of the rearrangement product, 0.32 g. of it was warmed with alcohol and dilute hydrochloric acid for half an hour, water was then added to the mixture and the precipitate which formed was collected and identified as benzophenone by its melting point,  $46$ – $48^{\circ}$ , which was not changed by the addition of synthetic benzophenone to the product. The filtrate from the benzophenone yielded aniline hydrochloride, which was converted into the chloroplatinate for analysis.

Subst., 0.1247, Pt 0.0404. Calc. for  $\text{C}_{12}\text{H}_9\text{N}_2\text{PtCl}_6$ : Pt, 32.78%. Found: 32.41.

The formation of phenylimidobenzophenone by the action of soda-lime on triphenylmethylbromoamine has thus been established beyond question

*2. By Treatment with Calcium Oxide.*—Some of the bromoamine (0.8 g.) was mixed with pulverized calcium oxide (0.8 g.) and the mixture gently heated in a hard glass test tube. The benzene extract was dried and evaporated *in vacuo*. Some of the yellow-brown substance obtained was

<sup>1</sup> Pauly, *Ann.*, 187, 198 (1877).

treated without further purification with hot dilute acid. The neutralized solution was tested with some calcium hypochlorite solution for aniline and the characteristic color reaction for aniline was shown intensely.

3. *By Treatment with Sodium Methylate.*<sup>1</sup>—Owing to the reducing power of sodium alcoholates and the sensitiveness of bromoamines to reducing agents, the rearrangement of triphenylmethylbromoamine by this reagent was expected to be accompanied by a partial reduction of the compound to triphenylmethylamine. Such a reduction does take place to a certain extent, but no difficulty was encountered in showing that a large part of the substance is rearranged when it is treated with a methyl alcohol solution of sodium methylate.

Two grams of bromoamine were added to a hot solution of sodium methylate, prepared from 1 g. sodium and 40 g. of methyl alcohol. The bromoamine melted, forming an oil which soon went into solution. In fifteen minutes a little of the solution gave the test for aniline, when treated as described above. The whole solution was then cooled and diluted with twice its volume of water. A yellow oil was formed which, on standing overnight, gave yellow crystals of phenylimidobenzophenone and a little of a white powder (benzophenone). The solids were treated with hot dilute acid and a small amount of recovered triphenylmethylamine hydrochloride was removed by filtration. Alkali was added to the solution and the aniline was distilled over with steam. Benzoyl chloride was added to the distillate and a white substance resulted, which on recrystallization gave 0.7 g. of benzanilide, melting at 158–160°. A mixture of the substance with synthetic benzanilide gave the same melting point.

The rearrangement also takes place if the bromoamine is added to a cold sodium methylate solution, but it is necessary to heat the mixture on the water bath for one-half hour instead of fifteen minutes, and the yield of benzanilide is not as good.

**Benzotriphenylmethylanide**,  $C_6H_5CO.NHC(C_6H_5)_3$ .—In order to become familiar with the properties of the benzoyl derivative of triphenylmethylamine itself, which might have been met with in the preceding experiment, it seemed best to prepare the compound. For this purpose, the amine (3 g.) was dissolved in 30 cc. of absolute ether and treated with a gram of benzoyl chloride. The mixture was shaken and allowed to stand for forty-eight hours. Since the odor of benzoyl chloride was still perceptible, the mixture was heated in a water bath with reflux for fifteen minutes. The ether was then filtered off and the precipitate dried. Two substances could be discerned: the hydrochloride of the amine and the benzoylated amine. Hot water removed the hydrochloride. Yellow crystals remained, a further portion of which was obtained by evaporation

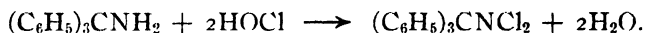
<sup>1</sup> Cf. Lengfeld and Stieglitz, *loc. cit.*

of the ether solution. Recrystallization of the product from alcohol gave white crystals melting at 160–162°.

Subst., 0.2619, cc. moist N, 23°, 752.7 mm.: 8.99. Calc. for  $C_{20}H_{21}NO$ : N, 3.86%. Found: 3.84.

**Triphenylmethyldichloroamine**,  $(C_6H_5)_3CNCl_2$ .—Hemilian and Silberstein<sup>1</sup> found that the passing of dry chlorine into a benzene solution of triphenylmethylamine gave ammonium chloride and triphenylmethylcarbinol. I obtained quite different results when the amine was treated with hypochlorous acid in an attempt to prepare the chloroamine corresponding to the bromoamine just described. It was found that a dichloroamine could readily be isolated. This compound apparently is more stable than the monochloroamine. Some monochloroamine is probably formed but it could not be isolated and identified despite many efforts to do so (see below). Berg<sup>2</sup> observed similar relations for chloroamines and dichloroamines of amines of the aliphatic series.

We have:



Hypochlorous acid was prepared according to Graebe's<sup>3</sup> method: the chlorine obtained from 13 cc. of concentrated hydrochloric acid and potassium permanganate (2 g.) was passed into an ice-cold solution of anhydrous sodium carbonate (3 g.) in 40 cc. of water. To this cold hypochlorous acid solution was added a solution of triphenylmethylamine (1 g.) in 5 cc. of alcohol and 10 cc. of water. This mixture was shaken for ten minutes in the freezing bath. Chloroform was then added to dissolve the white cheesy substance which had separated out, the chloroform solution was drawn off and the solvent evaporated in a blast of air. The addition of a little ligroin to the residue, and the continued scratching of the substance in the cold gave a white substance melting at 128°. This was analyzed iodometrically.

Subst., 0.0397 g. Cl, 0.00825. Calc. for  $C_{19}H_{18}NHCl$ : Cl, 12.09%;  $C_{19}H_{18}NCl_2$ : Cl, 21.64%. Found: 20.79.

Various attempts were made to prepare the monochloroamine by the mixing of theoretical amounts of the dichloroamine and the free base. Analysis and melting point determinations lead to the conclusion that if the monoderivative is formed at all, it is unstable, reverting to the amine and the dichloroamine.

**Rearrangements of Triphenylmethyldichloroamine.**—*I. By Heat.* Triphenylmethyldichloroamine (0.2 g.) was heated in a hard glass test tube to 132° in a metal bath. There was a slight explosion, and the odors of chlorine and hydrogen chloride and a penetrating odor, similar to that

<sup>1</sup> *Ber.*, 17, 757 (1884).

<sup>2</sup> *Ann. chim. phys.*, [7] 3, 289 (1894).

<sup>3</sup> *Ber.*, 35, 2754 (1902).



of isonitriles,<sup>1</sup> were detected. The contents of the tube were dissolved in alcohol, water and acid added and the solution heated on a water bath with reflux for one hour. A small amount of a dark brown oil separated. The solution was poured off from it, and the oil extracted with ether. On evaporation of the solvent the characteristic crystals of benzophenone were obtained, melting at 46°, alone, and when the crystals were mixed with synthetic benzophenone.

The acid solution was made alkaline, and again extracted with ether. Anhydrous oxalic acid was added to the dried extract and the oxalates of aniline and chloroaniline were precipitated. The mixture of oxalates was treated with cold water, the chloroaniline oxalate remaining undissolved. The oxalate solution when treated with alkali and chloride of lime solution gave a splendid aniline test. From the insoluble oxalate, treatment with alkali and ether gave *p*-chloroaniline melting, alone, at 67°, and at 69° when mixed with synthetic *p*-chloroaniline (m. p. 69°). With chloride of lime solution it produced a yellow color analogous to that obtained with *p*-chloroaniline. The formation of *p*-chloroaniline was evidently due to the chlorination of the phenyl group previous to, after, or during, its passage from the carbon to the nitrogen atom. The amount formed was very small.

2. *By Treatment with Soda-lime.*—The dichloride (0.2 g.) was intimately mixed with dry soda-lime (3 g.) and the mixture heated in a metal bath. At 132° a white smoke was given off, in which the odor of chlorine could be discerned. The benzene extraction of the residue was brown and on evaporation gave yellow-brown crystals. Recrystallization from hot absolute alcohol gave yellow crystals of phenylimidobenzophenone, melting at 109° alone, or at 110°, when mixed with the synthetic product. The soda-lime prevented any appreciable chlorination of a phenyl group, and no chloroaniline was obtained.

**Triphenylmethylchloromethylamine**,  $(C_6H_5)_3CNCl(CH_3)$ .—Triphenylmethylchloromethylamine was the next object of investigation with the view of determining whether the introduction of an alkyl radical into the amine group would prevent the rearrangement of a chloro- or bromoamine by interfering with the formation of a univalent nitrogen derivative.

Considerable difficulty was experienced in preparing methyltriphenylmethylamine from which the chloroamine has to be made. It was first made according to the method of Hemilian and Silberstein<sup>2</sup> by passing dry methylamine gas into a hot benzene solution of triphenylmethylchloride or bromide. The methylamine salt was removed by filtration and

<sup>1</sup> It will be recalled that a similar odor of isonitrile is observed when phenylhydroxylamine is heated. (Bamberger, *Ber.*, 32, 62; 33, 3605.) In both of these cases the odor may be due to a free univalent nitrogen derivative  $C_6H_5N:$  and  $(C_6H_5)_3CN$ .

<sup>2</sup> *Ber.*, 17, 745 (1884).

the filtrate evaporated to dryness. Recrystallization of the residue from alcohol gave a small yield of the amine and some ethoxytriphenylmethane  $(C_6H_5)_3COC_2H_5$ . With other solvents the yield was better but at no time was it very good. It was decided to try the preparation with sodium methylate and methylamine hydrochloride, following the method used successfully by Mothmer<sup>1</sup> and by Stieglitz and Leech<sup>2</sup> in the preparation of triphenylmethylhydroxylamine. Methylamine hydrochloride (2.9 g.) was added to a concentrated solution of sodium methylate obtained from sodium (1 g.) and methyl alcohol (9 g.). After the precipitation of sodium chloride, triphenylmethylchloride (4.6 g.) dissolved in benzene was added and the mixture shaken for one-half hour. The precipitated methylamine hydrochloride was recovered by filtration and the filtrate taken to dryness in a vacuum desiccator. This must be done slowly and with only a slight reduction of pressure, as the solution shows a great tendency to spatter. The residue was treated with dry ether and dry hydrogen chloride gas. A fine powder, triphenylmethylmethylamine-hydrochloride,  $(C_6H_5)_3CN(CH_3)H_2Cl$  (m. p.  $216^\circ$ ), was obtained. It was converted into the free base with potassium hydroxide solution and the base extracted with ether. Evaporation of the solvent gave a substance which on recrystallization from ligroin melted at  $73^\circ$ .<sup>3</sup>

For the conversion of the amine into the chloroamine, the hydrochloride (2 g.) was dissolved in 10 cc. of 50% alcohol and the solution poured into a hypochlorous acid solution made from 4 g. of chlorine and 6 g. of anhydrous sodium carbonate, to which had been added 2 g. of potassium carbonate. The cheesy substance formed was dissolved in chloroform, the solution was separated and brought to dryness in a desiccator. The residue was slightly yellow, but was not recrystallized. It melted at  $102-104^\circ$ .

Subst., 0.2777, Cl 0.03136. Calc. for  $C_{20}H_{18}NCl$ : Cl, 11.52%. Found: 11.30.

When hydrogen chloride gas was passed into an ether solution of the chloroamine, chlorine was given off and triphenylmethylmethylamine-hydrochloride was precipitated quantitatively. This proves the structure of the compound to be  $(C_6H_5)_3CNCl(CH_3)$ .

**Attempts to Rearrange Methyltriphenylmethylchloroamine.**—1. *By Heat.* Some of the chloroamine (0.4 g.) was placed in a hard glass test tube and heated in a metal bath. The substance melted at  $102^\circ$ ; the temperature was raised to  $130-135^\circ$  and maintained there for four minutes. On cooling, the slightly colored gum hardened; it was dissolved in ligroin and the original white substance melting at  $102-104^\circ$  was obtained in practically a quantitative yield. There were no signs of chemical action.

<sup>1</sup> *Ber.*, 37, 3152 (1904).

<sup>2</sup> *THIS JOURNAL*, 36, 272 (1914).

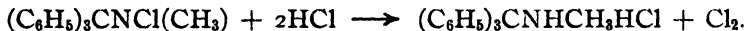
<sup>3</sup> Hemilian and Silberstein, *loc. cit.*, give the melting point as  $73^\circ$ .

2. *By Treatment with Soda-lime.*—Some of the methyltriphenylmethylchloroamine (0.6 g.) was mixed with powdered soda-lime (0.6 g.). The mixture was placed in a hard glass test tube and heated at 140° for five minutes. The only visible sign of reaction was the darkening of the soda-lime. When cool, water was added to the mixture, a part of the extract was made neutral and tested with calcium hypochlorite solution. No trace either of the purple test for aniline or of the blue color due to methylaniline<sup>1</sup> was observed. Nor was there any color reaction when the rest of the aqueous extract was boiled with acid, the solution made neutral and then tested as above.

The residue left by the water was boiled with dilute hydrochloric acid; a brown substance resulted which was contaminated with calcium oxide and melted at 184–190°. It was purified by treatment with potassium hydroxide solution, and extraction with ether. Hydrogen chloride gas was run into the ether extract, and a substance resulted, which melted at 216° when heated by itself or when mixed with methyltriphenylmethylamine hydrochloride. This shows that the chloroamine was converted back into the amine either by the action of the soda-lime



or by the subsequent action of hydrochloric acid,



No product of a rearrangement could, therefore, be detected.

3. *With Calcium Oxide.*—The methylchloroamine (0.5 g.) was mixed with powdered calcium oxide (0.6 g.) and treated as with soda-lime, save that the temperature was maintained at 130–140° for forty-five minutes. The tests with chloride of lime solution were made as previously and failed to show the slightest trace either of aniline or methylaniline. From the residue, methyltriphenylmethylamine was recovered as before. Therefore, no traces of any molecular rearrangement could be observed.

4. *By Destructive Distillation.*—Some of the methylchloroamine (0.6 g.) was placed in a small retort and heated in a metal bath. The end of the tube extended into acidulated water. At 180° the melted substance began to fume, and as the temperature was raised to 250° a gas was given off which smelled like hydrogen chloride. A part of the water solution was made neutral and tested with hypochlorite solution, but no indications of the presence even of traces of aniline or methylaniline were observed. The rest of the solution was evaporated, and no residue remained, which proved that the distillate contained no hydrochloride of aniline, methylaniline or methylamine.

The residue in the retort was heated with acid and part of it tested in slightly alkaline solution with chloride of lime solution. There were

<sup>1</sup> P. N. Leech, *THIS JOURNAL*, 35, 1042 (1913).

no color reactions. The remainder of the acid solution was treated with alkali and extracted with ether. The ether solution was saturated with hydrogen chloride gas, but there was no precipitate. It is evident that the compound was destroyed by heat, but there were no evidences of a molecular rearrangement leading to the formation of an aniline or methyl-aniline derivative.

***p*-Chlorophenyldiphenylmethylamine**,  $(p\text{-ClC}_6\text{H}_4)(\text{C}_6\text{H}_5)_2\text{CNH}_2$ .—The behavior of chlorophenyldiphenylmethylchloroamine was next investigated as a first step toward studying the influence of substitution groups in the phenyl groups in determining which of the aryl groups would pass from the carbon to the nitrogen in this rearrangement.

For the preparation of *p*-chlorophenyldiphenylmethylamine, which is not described in the literature, the corresponding chloride was first prepared according to the method of Gomberg<sup>1</sup> from benzophenonedichloride, chlorobenzene, and aluminium chloride. It was recrystallized from ligroin and melted at 86–89°.

Some of the substance (5.0 g.) was dissolved in hot benzene and dry ammonia gas was run into the solution. The addition of a little absolute alcohol aided the precipitation of ammonium chloride. After the treatment with ammonia gas had been continued for at least one-half hour, the solution was filtered and heated slightly to remove excess of ammonia gas; then dry hydrogen chloride gas was run into it. Part of the amine hydrochloride was precipitated, and the rest was obtained by evaporation of the benzene solution. A better yield resulted when the benzene solution saturated with ammonia gas was filtered to remove the ammonium chloride, the filtrate taken to dryness, the residue extracted with ether and the solution saturated with hydrogen chloride gas. The *p*-chlorophenyldiphenylmethylamine hydrochloride was precipitated, in part, and recovered in part by evaporation of the ether solution.

Some of the hydrochloride was treated with alkali to liberate the base; the ether extract of the latter gave a gum, which all attempts failed to convert into a crystallized solid. An analysis was, therefore, made of the hydrochloride, which was purified by conversion into the free base, the oxalate, the free base again and finally the hydrochloride. The latter melted at 185–186°. It was used for the preparation of the chloroplatinate; the latter was found to contain one molecule of water of crystallization and to melt at 155°.

Subst., 0.1587 g., heated three times, for five minutes each to 100–120° gave a constant weight of 0.1555 g. Calc. for 1 molecule  $\text{H}_2\text{O}$ :  $\text{H}_2\text{O}$ , 1.77%. Found: 2.01.

(Anhydrous) 0.1528: Pt, 0.0296. Calc. for  $\text{C}_{18}\text{H}_{14}\text{N}_2\text{Cl}_2\text{Pt}$ : Pt, 19.57%. Found: 19.37.

***p*-Chlorophenyl-diphenylmethyldichloroamine**,  $(\text{ClC}_6\text{H}_4)(\text{C}_6\text{H}_5)_2\text{CNCl}_2$ .—One gram of the amine hydrochloride was added to a mixture of two

<sup>1</sup> Ber., 39, 3278 (1906).

grams of potassium carbonate and of hypochlorous acid, prepared from 8 g. of anhydrous sodium carbonate dissolved in 150 cc. of water and treated with 5 g. of chlorine. The solution became milky as the hydrochloride dissolved. After the mixture had been shaken ten minutes in the freezing bath, chloroform was added to it to dissolve the semisolid mass. The evaporation of the chloroform left a gum, part of which dissolved in ligroin (b. p. 40-60°). The extract was placed in a stoppered tube and left in the icebox for three days. A white crystalline substance melting at 110-112° resulted. This was used for seeding subsequent preparations, and also for analysis.

Subst. 0.1321, active<sup>1</sup> chlorine 0.02578. Calc. for  $C_{19}H_{14}Cl.NHCl$ : Cl, 10.84%;  $C_{19}H_{14}Cl.NCl_2$ : Cl, 19.56%. Found: Cl, 19.51.

**Rearrangement of *p*-Chlorophenyl-diphenylmethyldichloroamine.—**

1. *By Heat.* A little of the substance was heated to 150°, at which temperature there was a sudden evolution of yellow smoke. When the resulting product was tested in the usual way, after it had been heated with acid, the characteristic aniline test was observed. No further test was made of this product.

2. *By Soda-lime.*—The main experiments were performed with soda-lime in order to prevent the formation of any chloroaniline by chlorination. The reaction was carried out in the same way as described for triphenylmethyldichloroamine. The mixture was heated to 150°, the benzene extract saturated with hydrogen chloride and taken to dryness. It was then heated with alcohol and dilute hydrochloric acid for ten minutes, and shaken with ether to remove the benzophenone and chlorobenzophenone formed by the hydrolysis of the imido ketones. Potassium hydroxide solution was added to the water solution and the alkaline mixture extracted with ether. Anhydrous oxalic acid was added to the dried ether solution and the oxalates of aniline and chloroaniline obtained as a white precipitate. This was dissolved in the least amount of hot water and the solution then cooled to 40°. The precipitate of *p*-chloroaniline oxalate, which formed, was decomposed by alkali and chloroaniline extracted with ether. *p*-Chloroaniline resulted, melting at 67° alone and at 69° when mixed with the pure product (m. p. 69°). It gave a yellow-red-brown color with hypochlorite in the same way as pure *p*-chloroaniline does.

The dissolved aniline oxalate gave the characteristic aniline color reaction with hypochlorite.

**Determination of the Proportion of Aniline and Chloroaniline Formed.<sup>2</sup>**

—Two experiments were performed to determine the proportion of phenyl-

<sup>1</sup> Only two of the three chlorine atoms are determined, they being active toward the iodide which was used in the analysis.

<sup>2</sup> The method of analysis used was worked out by Stieglitz and Leech, *loc. cit.*, for the study of the rearrangement of the corresponding chlorophenyl-diphenylmethylhydroxylamine.

imidochlorobenzophenone and chlorophenylimidobenzophenone formed by the migration of the  $(C_6H_5)$  and  $(ClC_6H_4)$  radicals, respectively, from carbon to nitrogen in the molecular rearrangement of the chloroamine as induced by soda-lime. The reaction and subsequent treatment were carried out as described above, save that the two anilines were precipitated as hydrochlorides instead of as oxalates, the precautions given by Leech being observed. From 0.5 g. of the dichloroamine, 0.1 g. of mixed dry hydrochlorides was obtained. The proportion of aniline and chloroaniline was found by Curme's bromination method.<sup>1</sup>

Subst., 0.0689, 0.0528; cc. 0.1  $N$   $KBrO_3$  27.30, 20.97. Found: Aniline, 74.2, 76.6 molar per cent., chloroaniline 25.8, 25.4.

**An Attempt to Effect the Rearrangement of Benzophenonechloroimide,**  $(C_6H_5)_2C : NCl$ .<sup>2</sup>—It was hoped that chlorine might be absorbed by benzophenonechloroimide to form a substance,  $(C_6H_5)_3CCl.NCl_2$ , similar in structure to  $(C_6H_5)_3CNCl_2$ , which might rearrange at a high temperature, and produce benzchloroanilide,  $C_6H_5CCl : NC_6H_5$ , by a series of reactions discussed in the theoretical part of the paper. The chloroimide was prepared in the way described by P. P. Peterson<sup>3</sup> and melted at  $37^\circ$ .

Five attempts were made to rearrange this product but all were unsuccessful. For the sake of future workers in this field, the experiments will be described briefly to indicate the path followed. After each attempt the substance was tested in the following ways: (a) It was boiled with acid, the solution was made neutral and hypochlorite solution was added. A color reaction would have indicated the presence of aniline or chloroaniline.

(b) The substance was heated with soda-lime and then boiled with acid. The mixture was made neutral and tested with hypochlorite solution as above. The treatment with soda-lime was applied because benzochloroanilide on hydrolysis would give benzanilide which does not show the aniline test until it has been decomposed by soda-lime.

1. Dry chlorine gas was passed for one-half hour over the chloroimide (0.5 g.) maintained at a temperature of  $130$ – $140^\circ$  in a metal bath. When cooled, the product was the unchanged compound melting at  $37^\circ$ . It gave no test for the anilines.

2. The second and third experiments were similar and were as follows: The chloroimide (0.5 g.) was placed in a small tube and dry chlorine gas was run into the tube for fifteen minutes. The substance became yellow, and melted slightly. The tube was sealed, and heated for two hours in a furnace at  $150^\circ$ . When cool, some of the substance was removed and treated as described above. It gave no test for the anilines,

<sup>1</sup> THIS JOURNAL, 35, 1143 (1913).

<sup>2</sup> See p. 2083.

<sup>3</sup> Stieglitz and Peterson, *Ber.*, 43, 782 (1910); Peterson, *Am. Chem. J.*, 46, 325 (1911).

3. Chloroimide (0.5 g.) was dissolved in ether and phosphorus pentachloride (0.5 g.) was added to the mixture. This was heated with reflux for two hours. The precipitate was filtered off, and proved to be the imido-hydrochloride,  $(C_6H_5)_2C = NH_2Cl$ . When tested, no color reactions were observed.

4. The fifth attempt to effect the rearrangement of benzophenone-chloroimide was similar to the second and third attempts, except that the closed tube was heated to  $230^\circ$  for two hours. The substance was colored owing to decomposition, but no trace of aniline or chloroaniline could be observed.

Although this work was negative in regard to the formation of benzo-chloroanilide by rearrangement, the results are of interest, in that they emphasize the remarkable difference in behavior of  $(C_6H_5)_3CNHCl$  and  $(C_6H_5)_2C : NCl$  and that they bring additional evidence against the theory by some chemists that  $R_2C = NCl$  is an intermediate product in the rearrangement of  $R_2C = NOH$  to  $R.CCl(:NR)$  by means of phosphorus pentachloride.

CHICAGO, ILL.

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

## THE MOLECULAR REARRANGEMENT OF SOME TRIARYLMETHYLCHLOROAMINES.<sup>1</sup>

BY AGNES FAY MORGAN.

Received August 1, 1916.

Three series of triphenylmethane derivatives have been found, in this laboratory, to undergo molecular rearrangements akin to each other and quite analogous to the Lossen-Curtius-Hofmann-Beckmann rearrangements of acid and ketone derivatives.<sup>2</sup> Triphenylmethylhydroxylamines rearrange under the influence of phosphorus pentachloride,<sup>3</sup> triphenylmethylchloroamines rearrange under the influence of alkaline reagents,<sup>4</sup> and, according to recent work, triphenylmethyl azides also undergo rearrangement under the influence of heat.<sup>5</sup> In all three series the same products of rearrangement are obtained, a result which we may most easily interpret on the basis of Stieglitz's theory of the intermediate formation

<sup>1</sup> The work presented in this paper is used in a dissertation presented to the University of Chicago in part fulfillment of the requirements for the Ph.D. degree.

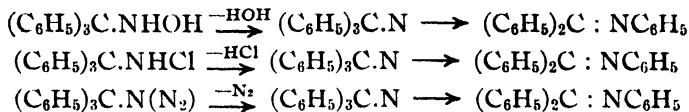
<sup>2</sup> See the literature references in an article by Stieglitz and Leech, *THIS JOURNAL*, 36, 272 (1914).

<sup>3</sup> Stieglitz, Reddick and Leech, *8th Intern. Congr. Appl. Chem.*, 25, 443 (1912); Stieglitz and Leech, *Ber.*, 46, 2147 (1913); *THIS JOURNAL*, *loc. cit.*

<sup>4</sup> Stieglitz and Vosburgh, *Ber.*, 46, 2151 (1913), and unpublished work of Isabella Vosburgh, 1913.

<sup>5</sup> Unpublished work by J. K. Senior, 1913-1914.

of a univalent nitrogen derivative. In the first series, this product is formed by the loss of water through the action of phosphorus pentachloride, in the second one through the loss of halogen acid by the action of the alkali used, and in the final series through the loss of nitrogen under the influence of heat. We have, thus:



When substituted triphenylmethane derivatives, such as  $(\text{XC}_6\text{H}_4)(\text{C}_6\text{H}_5)_2\text{C.NHCl}$ , are employed, mixtures are obtained, containing some  $(\text{C}_6\text{H}_5)_2\text{C} : \text{NC}_6\text{H}_4\text{X}$  and some  $(\text{XC}_6\text{H}_4)(\text{C}_6\text{H}_5)_2\text{C} : \text{NC}_6\text{H}_5$ . It seemed an interesting question to determine in each of the series the ratios in which these products are formed, since such determinations might throw light on the mechanism of the rearrangements, especially on the question whether the same intermediate product  $(\text{XC}_6\text{H}_4)(\text{C}_6\text{H}_5)_2\text{C.N}$ , yielding the same proportions of the above two derivatives, may be considered to be the real rearranging substance in all three cases. For this purpose it was necessary to follow, quantitatively, the rearrangement in a number of cases in which X is varied. For the chloroamines, Miss Vosburgh examined the monochlorine derivative. In continuation of her work, I have, at the suggestion and under the direction of Professor Stieglitz, studied the behavior of two further derivatives of this series, dichlorophenylphenylmethylchloroamine and chlorophenylbromophenylphenylmethylchloroamine. Mr. Stagner has determined the ratios of the products formed for the corresponding hydroxylamine derivatives.<sup>1</sup>

### Experimental Part.

**Di-*p*-chlorophenyl-phenylmethaniminehydrochloride**,  $(\text{ClC}_6\text{H}_4)_2(\text{C}_6\text{H}_5)\text{C.NH}_2\text{Cl}$ .—For the preparation of di-*p*-chlorophenyl-phenylmethylchloroamine it was necessary to obtain the amine itself from the corresponding triaryl methylchloride. For this purpose di-*p*-chlorobenzophenone was first prepared through the condensation of carbon tetrachloride and chlorobenzene with the aid of aluminium chloride at ordinary temperature, the reaction described by Norris and Twiege<sup>2</sup> being followed. The mixture of dichlorobenzophenones was recrystallized from hot dilute alcohol, and then from warm ligroin (40 to 60°). Di-*p*-chlorobenzophenone was obtained as a glistening flaky crystalline substance which melted at 144°. The ortho-ortho and ortho-para forms of the dichlorobenzophenone are very much more soluble in alcohol and in ligroin than the para-para compound, and the separation is thus made almost quantitatively.

<sup>1</sup> The results obtained in the different groups of triphenylmethyl derivatives will be compared with one another by Professor Stieglitz.

<sup>2</sup> *Am. Chem. J.*, **30**, 392 (1903).



The *di-p*-chlorobenzophenone thus obtained was next converted into *di-p*-chlorophenylphenyl carbinol by the method of Gomberg and Cone<sup>1</sup> by means of the Grignard reaction. The resulting yellow gum crystallized at once from cold ligroin (40 to 60°). On recrystallization several times from ligroin a product melting at 87° was obtained.<sup>2</sup>

From the carbinol the *p,p'*-dichlorophenylphenylmethylchloride was prepared in carbon disulfide solution by saturation with anhydrous hydrogen chloride. The chloride made in this way remained as a yellowish semisolid gum when the carbon disulfide was removed.<sup>3</sup> It was, however, quite pure, as shown by the hydrolysis of a weighed portion in alcohol with an excess of 0.1 *N* alkali and titration of the excess with 0.1 *N* hydrochloric acid.

Subst. 0.5035 g.; cc. of 0.1 *N* KOH, 14.39. Calc. for (C<sub>13</sub>H<sub>13</sub>Cl<sub>2</sub>)Cl: 10.20% hydrolyzable Cl. Found: 10.13%.

The chloride was converted into the amine by means of ammonia. The chloride (2 g.) was dissolved in hot benzene, and dry ammonia gas from a liquid ammonia tank passed into the solution, for at least half an hour. After the first twenty minutes a small quantity of absolute ethyl alcohol was added through the reflux condenser, to aid in the precipitation of ammonium chloride. The precipitated salt was at once filtered off and the clear benzene solution of the dichlorophenylphenylmethylamine evaporated on an electric plate. The gum remaining was dissolved in absolute ether and the solution saturated with dry hydrogen chloride. Most of the amine hydrochloride was at once precipitated, and the rest recovered by evaporation of the solution to dryness, the residue being washed with a little absolute ether. By this method 75% of the theoretical yield of the hydrochloride was obtained. The substance was purified by solution in chloroform and fractional precipitation with low-boiling ligroin. The purest product melted at 201°. For the analysis a weighed portion of the hydrochloride was dissolved in alcohol, an excess of 0.01 *N* NaOH was added, and the excess titrated with 0.01 *N* HCl, phenolphthalein being used as the indicator.<sup>4</sup>

Subst. 0.0381 g.; cc. of 0.01 *N* NaOH, 10.18. Calc. for (C<sub>13</sub>H<sub>13</sub>Cl<sub>2</sub>N)HCl: HCl 10.00%. Found: 9.74%.

***p*-Dichlorophenyl-phenylmethylchloroamine**, (ClC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>)CNHCl. —The dichlorophenyl-phenylmethylchloroamine was prepared from the amine hydrochloride by treatment with sodium hypochlorite. The

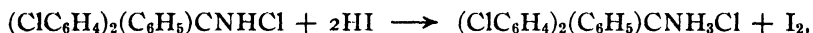
<sup>1</sup> *Ber.*, 39, 3280 (1906); cf. Stagner, *THIS JOURNAL*, 38, 2069 (1916).

<sup>2</sup> Gomberg and Cone found the same melting point for the purest dichlorophenylphenyl carbinol made by them.

<sup>3</sup> Stagner, *loc. cit.*, obtained the chloride in crystallized form by allowing the gum to stand a month.

<sup>4</sup> For this analysis special carbondioxide-free reagents and special apparatus were used, prepared by S. D. Wilson for measurements of velocities of saponification.

hypochlorite solution was prepared by Graebe's method by passing chlorine (from 5 g. of potassium permanganate and 40 cc. of concentrated hydrochloric acid) into an ice-cold solution of sodium carbonate (8 g.). The dichlorophenylphenylmethylamine hydrochloride (1 g.), dissolved in 2 or 3 cc. of chloroform, and potassium carbonate (2 g.) were added to the hypochlorite solution, and the mixture stirred with a Schultze stirrer at  $-2^{\circ}$  for ten minutes. The chloroform solution of the chloroamine was then separated from the aqueous mixture by means of a separating funnel, and dried with a little granular calcium chloride. The solvent was then removed in a blast of dry air, and the gum remaining extracted with low-boiling ligroin. Most of the ligroin was driven off by air also and the last traces removed by prolonged drying in a vacuum desiccator. The chloroamine formed at first a thick, viscous yellow gum which dried to a hard, varnish-like substance that could be pulverized. The solid melted at  $55^{\circ}$ . A weighed portion of the substance was dissolved in a little alcohol, small quantities of acetic acid and of a 5% solution of potassium iodide were added, and the iodine, released according to the equation



was titrated with 0.1 *N* thiosulfate solution. No starch was used, the yellow color of the iodine giving a perfectly satisfactory end point.

Subst. 0.2032 g.; 0.0649; cc. of 0.1 *N*  $\text{Na}_2\text{S}_2\text{O}_3$ , 11.02, 3.39. Calc. for  $(\text{C}_{13}\text{H}_{13}\text{Cl})\text{-NHCl}$ : active Cl, 9.78%. Found: 9.61, 9.26.

It was evident from the analysis that the monochloroamine was formed in this case. With chlorophenyldiphenylmethylamine, Miss Vosburgh<sup>1</sup> found that the formation of the dichloroamine was favored, and the monochloroamine could not be obtained by her.

**Rearrangement of *p,p'*-Dichlorophenyl-phenylmethylchloroamine.**—In order to effect the rearrangement of the chloroamine, soda lime (2 g.) was heated with the chloroamine (1 g.) for five minutes in a metal bath at 160 to 180°. As the chloroamine was obtained chiefly as a sticky solid gum, the mixture with soda lime was best prepared by allowing the ligroin solution of the gum to evaporate to dryness, after it had been mixed with soda lime in an Erlenmeyer flask. The mixture when heated turned yellow, the color of the phenylimidobenzophenones. The mass was extracted with several portions of benzene and the benzene solution filtered and evaporated to dryness. The resulting gum, consisting of a mixture of phenylimido-*p*-dichlorobenzophenone and *p*-chlorophenylimido-*p*-chlorobenzophenone, was hydrolyzed at once by solution in a little alcohol, and by being heated with a small amount of dilute hydrochloric acid for fifteen minutes. After evaporation of the alcohol, the ketones were extracted with ether and the aqueous solution examined for the hydrochlorides of aniline and *p*-chloroaniline.

<sup>1</sup> Isabella Vosburgh, *THIS JOURNAL*, 38, 2081 (1916).

**Identification of *p*-Chlorobenzophenone and *p,p'*-Dichlorobenzophenone.**—The ether extract of the hydrolyzed mixture described above was spontaneously evaporated, and the resulting flaky crystals recrystallized from alcohol. Enough alcohol was added to dissolve about three-fourths of the entire mass, the residue was collected and dissolved in a small amount of hot alcohol. The few crystals precipitated on cooling, were collected on a Hirsch filter and dried *in vacuo*. The melting point of this substance was  $141^{\circ}$ . *p,p'*-Dichlorobenzophenone melts at  $144^{\circ}$ , and a mixture of the product obtained with some synthetic substance melted at  $141^{\circ}$ , which proved the identity of the isolated ketone. The alcoholic filtrate was allowed to evaporate spontaneously, the residue taken up with a few drops of alcohol, the solution decanted through a cotton filter, the filtrate evaporated almost to dryness, and the remaining few drops of solution decanted from a small crystalline residue. When dried, this melted at  $77$  to  $78^{\circ}$ ; *p'*-chlorobenzophenone, according to different authors, melts at  $74$  to  $78^{\circ}$ , and a mixture of some synthetic substance (m. p.  $74^{\circ}$ ) with the product isolated as described, melted at  $74^{\circ}$ .

**Identification of Aniline and *p*-Chloroaniline.**—The aqueous solution recovered from the hydrolysis of the rearranged product was placed in a separatory funnel, strong sodium hydroxide solution and solid sodium chloride added to it, and the liberated aniline and *p*-chloroaniline extracted with two portions of ether. An ether solution of hydrogen chloride was used to form aniline hydrochloride and *p*-chloroaniline hydrochloride. As the hydrochlorides are somewhat soluble in ether containing hydrogen chloride, most of the ether was driven off on the electric oven, and the hydrochlorides finally dried over solid potassium hydroxide *in vacuo*. Part of the dry salts was dissolved in water and on the addition of a few drops of concentrated ammonium hydroxide, *p*-chloroaniline separated out in white crystals. The difference in solubility in water of aniline and *p*-chloroaniline was great enough to secure an almost perfect separation. The *p*-chloroaniline thus obtained melted at  $69.5^{\circ}$  and mixed with pure synthetic *p*-chloroaniline (m. p.  $70.5^{\circ}$ ) melted at  $70.5^{\circ}$ . The filtrate gave a strongly positive test for aniline when tested with bleaching powder solution in the usual way.

**Proportion of Aniline to *p*-Chloroaniline.**—From two grams of the rearranged substance 0.6 g. of the mixed aniline hydrochloride and *p*-chloroaniline hydrochloride was obtained as described above. A weighed portion was analyzed by the bromination method of Curme<sup>1</sup> for the determination of the proportion of aniline and chloroaniline present.

The calculation is made with the aid of the simultaneous equations  $0.1295x + 0.164y = a$  and  $60x + 40y = b$ , when  $x$  and  $y$  represent, respectively, the millimols of aniline hydrochloride and *p*-chloroaniline hydrochloride present,  $a$  the weight of the mixture of salts used, and  $b$  the number of cubic centimeters of 0.1 *N*  $\text{KBrO}_3$  used.

<sup>1</sup> THIS JOURNAL, 35, 1143 (1913).

Subst. 0.0382, 0.0556, 0.242; cc. of 0.1 *N* KBrO<sub>3</sub>, 11.54, 16.88, 7.41. Found, in molar %: C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>Cl, 31.4, 32.1, 33.2; ClC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>Cl, 68.6, 67.9, 66.8.

***p*-Chlorophenyl-*p*-bromophenyl-phenylmethylaniline Hydrochloride**, (ClC<sub>6</sub>H<sub>4</sub>)(BrC<sub>6</sub>H<sub>4</sub>)(C<sub>6</sub>H<sub>5</sub>)NH<sub>2</sub>Cl.—For the preparation of this compound a start was made from *p*-chlorobenzophenone, obtained from chlorobenzene and benzoyl chloride with the aid of aluminium chloride: the ketone first obtained was semisolid and was distilled at 220° at 35 mm. pressure, and recrystallized from hot alcohol. The ketone then melted at 74°. The yield was 80% of the theoretical amount. This *p*-chlorobenzophenone was converted into the ketone dichloride,<sup>1</sup> which was purified by distillation under reduced pressure, as directed by Overton.<sup>2</sup> The fraction of the oil used distilled at 190° at 10–12 mm. pressure and gave, by hydrolysis, 26.02% HCl (theory 26.12%). The yield of purified dichloride was 90% of the theoretical.

The dichloride was converted into *p*-chlorophenyl-*p*-bromophenyl-phenylcarbinol in the way described by Stagner.<sup>3</sup> The carbinol was found to be more difficult to crystallize than the corresponding dichloroderivative and recourse was had to the method described by Gomberg and Cone<sup>3</sup> for the crystallization of the latter compound. Anhydrous ferric chloride in ethyl acetate solution in molecular proportions was added to an ethyl acetate solution of the carbinol. The resulting ferric salt crystallized out in glistening greenish scales which yielded a yellowish oil on hydrolysis. This oil was easily converted into crystals by solution in warm ligroin (70 to 80°); after purification by recrystallization the compound melted at 92°. The chloride was obtained from this carbinol by saturation of a dry carbon disulfide solution of the latter with hydrogen chloride. Without further purification, this *p*-chlorophenyl-*p*-bromophenylphenylmethyl chloride was treated with ammonia in benzene solution as described for the dichloro compound and from the product the amine hydrochloride was precipitated from its solution in ether. The hydrochloride was purified by precipitation by ligroin out of chloroform solution, and was found to melt at 196°.

Subst. 0.1019; cc. of 0.01 *N* NaOH, 25.42. Calc. for (C<sub>15</sub>H<sub>13</sub>ClBrN)HCl: HCl, 8.91%. Found: 9.10%.

***p*-Bromophenyl-*p*-chlorophenyl-phenylmethylchloroamine**, (ClC<sub>6</sub>H<sub>4</sub>)(BrC<sub>6</sub>H<sub>4</sub>)(C<sub>6</sub>H<sub>5</sub>)CNHCl.—The amine hydrochloride, dissolved in chloroform, was stirred with an ice-cold solution of sodium hypochlorite and potassium carbonate exactly as described above for the dichloro substance. The chloroamine, purified by extraction with ligroin, remained in a semi-solid condition. It was dissolved in alcohol and analyzed iodometrically.

<sup>1</sup> Cf. Mackenzie, *J. Chem. Soc.*, 69, 987 (1896).

<sup>2</sup> *Ber.*, 26, 28 (1893).

<sup>3</sup> *Loc. cit.*

Subst. 0.1722, 0.0950; cc. of 0.1 *N* Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, 7.80, 4.62. Calc. for (C<sub>18</sub>H<sub>13</sub>ClBr)-NHCl: active Cl, 8.71%. Found: 8.03, 8.62.

**Rearrangement of *p*-Bromophenyl-*p*-chlorophenyl-phenylmethyl-chloroamine.**—This substance was heated with soda-lime in a metal bath at 200 to 210° for five minutes in order to effect its rearrangement. The extraction with benzene was carried out as explained before and the hydrolysis of the resulting mixture of arylimidobenzophenones yielded a mixture of ketones (*p*-chlorobenzophenone, *p*-bromobenzophenone, and *p*-bromo-*p*-chlorobenzophenone) and an aqueous solution of the hydrochlorides of *p*-chloroaniline, *p*-bromoaniline, and aniline. This mixture of the aniline hydrochlorides was made alkaline and extracted with ether, and the hydrochlorides reprecipitated with a freshly made solution of hydrogen chloride in absolute ether. The resulting crystalline mass was further purified by precipitation by ether from absolute alcohol solution and the product and then carefully dried *in vacuo*.

The proportions of aniline, *p*-chloroaniline, and *p*-bromoaniline in the hydrolyzed product of the above rearrangement were found by determinations of the hydrochloric content of, and the bromine absorbed by, a definite weight of the mixed hydrochlorides.

We have then the three simultaneous equations,  $0.1295x + 0.164y + 0.208z = a$ ;  $60x + 40y + 40z = b$ ; and  $x + y + z = c$ . In these equations, *x*, *y* and *z* represent, respectively, the millimols of aniline hydrochloride, chloroaniline hydrochloride and bromoaniline hydrochloride present in a given weight *a* of the mixed salts, *b* is the number of cc. of 0.1 *N* KBrO<sub>3</sub> used to brominate the salts, and *c* represents the number of cc. of *N* NaOH (1/100 of the volume of 0.01 *N* solution actually used) required to neutralize the same weight of the mixed hydrochlorides. In carrying out the determinations, the titration with alkali is made first, phenolphthalein being the indicator, and the same solution is used for the bromination process. In view of the determinations representing an indirect method for three unknown components, the molecular weights of two of which are not very far apart, the method gives only approximate results.

Subst. 0.0315, 0.0262 and 0.0573 g.; cc. of 0.1 *N* KBrO<sub>3</sub>, 9.11, 7.47, 15.23; cc. of 0.01 *N* NaOH, 19.35, 15.94, 33.14.

	Molar percentages.			Average.
Aniline hydrochloride.....	35.3	34.4	29.8	33
Chloroaniline hydrochloride.....	40.0	38.10	27.0	35
Bromoaniline hydrochloride.....	24.7	27.5	43.2	32

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF CORNELL UNIVERSITY.]

## DIETHYLAMINO-*m*-HYDROXYBENZOYL TETRACHLOROBENZOIC ACID AND TRICHLORODIETHYLAMINOXANTHONE-CARBOXYLIC ACID AND SOME OF THEIR DERIVATIVES.

BY W. R. ORNDORFF AND C. C. ROSE.

Received August 3, 1916.

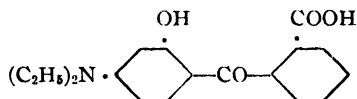
### Historical.

Diethylamino-*m*-hydroxybenzoylbenzoic acid is first mentioned by Graebe, Kohn and Huguenin.<sup>1</sup> They obtained it by fusing tetraethylrhod-

<sup>1</sup> *Archives des sciences physiques et naturelles de Genève*, 2, 91 (1893).

amine with soda, the decomposition of the rhodamine being analogous to that of fluorescein into dioxybenzoylbenzoic acid<sup>1</sup> (page 2115).

In 1896, a German patent was granted the Basler Chemical Company covering a method of preparing new condensation products from phthalic acid anhydride and the dialkylmetamino-phenols.<sup>2</sup> This method, as applied to the diethyl acid, is as follows: 15 kg. of phthalic acid anhydride are dissolved in 75 kg. of toluene and 16.5 kg. of diethyl-*m*-aminophenol added. The solution is boiled for several hours, until there is no further increase in the crystalline precipitate, which separates after some time. The product is purified by crystallization from alcohol. It behaves like an amino acid, since it forms salts with both bases and mineral acids. The melting point cannot be sharply determined. Above 180°, it decomposes forming a red liquid. From the method of formation and the properties of the compound, the following formula is given to it:



Later the Basler Chemical Company was granted another patent<sup>3</sup> covering a new method for the preparation of this compound as follows: 17 kg. of diethyl-*m*-aminophenol are melted at 100° and 15 kg. of phthalic acid anhydride added. The temperature is held at 100° until the mass completely solidifies. It is then extracted with a small quantity of alcohol and the residue purified by crystallization from alcohol.

Haller and Guyot<sup>4</sup> were the first to make a scientific investigation of this compound. They prepared it according to the patents of the Basler Chemical Company and describe it as being made up of small white needles which decompose at 203° and which are but slightly soluble in alcohol even on warming.

Haller and Umbgrove<sup>5</sup> describe later the preparation of *p*-diethyl-aminobenzoyltetrachloro-*o*-benzoic acid,



With acetic anhydride, this acid gave a mixed anhydride, to which they assign the formula



They state that the acid cannot be esterified by the ordinary method and they prepared the esters by heating the mixed anhydride with sodium alcoholate.

<sup>1</sup> Baeyer, *Ann.*, **183**, 23 (1876).

<sup>2</sup> D. R. P. 85931, *Frdl.*, **4**, 260.

<sup>3</sup> D. R. P. 87065, *Ibid.*, **4**, 262.

<sup>4</sup> *Compt. rend.*, **126**, 1248 (1898).

<sup>5</sup> *Bull. soc. chim.*, **25**, 598 (1901).

Later the same authors<sup>1</sup> prepare diethylamino-*m*-hydroxybenzoyltetrachlorobenzoic acid according to the German patent 87068. Diethyl-*m*-aminophenol is melted on the water bath and the calculated amount of tetrachlorophthalic acid anhydride added. At the end of three hours the reaction is complete. It is brought about more rapidly when the temperature of the mixture is raised to 150° and the mass is stirred. The product is extracted with a small quantity of alcohol to dissolve any tetrachlororhodamine formed, and the products not entering into the reaction. Crystallized from alcohol it melts at 198° to a red liquid. Analyses gave the following results:

Calc. for  $C_{18}H_{15}Cl_4NO_4$ : C, 47.89; H, 3.32; N, 3.10; Cl, 31.48. Found: C, 47.76; H, 3.53; N, 3.27; Cl, 31.30 (page 2106).

In 1901, a patent<sup>2</sup> was granted to the Farbwerke vormals Meister, Lucius und Brüning covering the preparation of phthalic acid dyes of the naphthalene series, in which is described the preparation of diethylaminohydroxybenzoyldichloro- and -tetrachlorobenzoic acids.

For the former, 108 parts of dichlorophthalic acid anhydride, 82.5 parts of diethyl-*m*-aminophenol and 650 parts of toluene are heated to boiling for about 10 hours. The product is freed from toluene, dissolved in soda solution (93 g.  $Na_2CO_3$  to one liter  $H_2O$ ) and the solution heated. On cooling, an oil separates consisting of the sodium salt of the new acid and the diethyl-*m*-aminophenol not entering into the reaction. It is purified by dissolving in water, precipitating with sodium carbonate, redissolving in water and extracting the diethyl-*m*-aminophenol with ether. The dichloro acid precipitated out of the solution of the sodium salt by acetic or hydrochloric acid is amorphous, insoluble in water, soluble in alcohol and chloroform, and, in the pure condition, in excess of sodium carbonate solution without the separation of the oily sodium salt.

The tetrachloro acid is prepared from tetrachlorophthalic acid anhydride and diethyl-*m*-aminophenol in the same way as the dichloro acid and is like the latter in nearly all respects, only it is far more difficultly soluble in chloroform. It forms a sodium salt that even in the pure condition separates as an oil on the addition of excess of sodium carbonate solution.

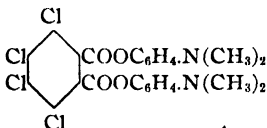
Bloch<sup>3</sup> in 1913 prepared *dimethylamino-m*-hydroxybenzoyltetrachlorobenzoic acid by heating equal molecules of *dimethylmetaminophenol* and tetrachlorophthalic acid anhydride in xylene. The solvent was distilled off, the material dissolved in sodium carbonate solution, precipitated by a dilute acid and purified by crystallization from acetic acid or dilute alcohol.

<sup>1</sup> *Bull. soc. chim.*, **25**, 747 (1901).

<sup>2</sup> D. R. P. 118077, *Frdl.*, **6**, 276.

<sup>3</sup> *Bull. de la Société Industrielle de Mulhouse*, **83**, 81 (1913).

He states that "besides the benzoylbenzoic acid, the presence of a yellow colored derivative was observed, insoluble in alkalis and which gave a colorless salt with hydrochloric acid. It crystallized from glacial acetic acid in yellow needles." He gives no analysis of this product, but thinks it may result from the esterification of dimethyl-*m*-aminophenol with tetrachlorophthalic acid anhydride (page 2113).



This investigation was undertaken for the purpose of determining the best conditions for preparing diethylamino-*m*-hydroxybenzoyltetrachlorobenzoic acid and to study its properties, chemical reactions and some of its derivatives. It seems probable that this acid is an intermediate product in the formation of tetrachlororhodamine and hence it was thought that its study would throw some light on this important class of dyes.

### Experimental.

In the following pages all chlorine determinations were made by the lime method.<sup>1</sup> The nitrogen determinations were made by the Kjeldahl method, with the added precaution that the digestion was extended over a period of about three hours after the solution had become colorless. This was to insure complete transformation of all the nitrogen to ammonia, as nitrogen which splits off from a compound as an amine (diethylamine in this case) is difficultly transformed into ammonia in the Kjeldahl reaction. The drying tube used to bring the substances to constant weight was the electrically heated one described by Chamot and Pratt,<sup>2</sup> and more in detail by Orndorff and Nichols.<sup>3</sup> As most of the compounds described have decomposition points instead of melting points, and these show a tendency to vary with the speed of heating, it might be well to say here that the temperatures of decomposition were determined in an electrically heated Thiele apparatus which was so regulated as to give a rise in temperature of about 1° in 3 seconds. All temperatures of decomposition and melting points given, are uncorrected.

The diethyl-*m*-aminophenol used was very kindly furnished by the Badische Anilin- und Soda-Fabrik. It was in dark colored lumps but quite pure. Just before using it was always purified by distillation in a vacuum, as described by Meyenburg.<sup>4</sup> When exposed to the air, it quickly reddens. In order to determine its purity it was distilled under reduced pressure, the receiver being changed after the temperature had

<sup>1</sup> *Am. Chem. J.*, **41**, 397 (1909).

<sup>2</sup> *J. Am. Chem. Soc.*, **32**, 635 (1910).

<sup>3</sup> *Am. Chem. J.*, **48**, 477 (1912).

<sup>4</sup> *Ber.*, **29**, 502 (1896).



become constant, and a nitrogen determination was made on the second fraction.<sup>1</sup>

Subst., I, 0.3659; II, 0.6142; cc. 0.1 *N* HCl, I, 21.10; II, 37.89.

Calc. for  $\text{HO.C}_6\text{H}_4\text{N(C}_2\text{H}_5)_2$ : N, 8.48%. Found: N, I, 8.08; II, 8.64.

The sulfuric acid became colorless after digesting for one hour. The first determination was stopped at this point while the second was run for three hours longer.

The tetrachlorophthalic acid anhydride was prepared by heating pure tetrachlorophthalic acid to 105°. The purity of the anhydride was checked by molecular weight determinations, made by titrating a weighed sample with standard alkali.<sup>2</sup>

Subst., I, 0.1304; II, 0.1774; cc. 0.1 *N* NaOH, I, 9.13; II, 12.42.

Calc. for  $\text{C}_6\text{Cl}_4\text{O}_3$ : M. W. 285.8. Found: I, 285.7; II, 285.8.

**Hydroxyphenyldiethylammoniumdiethylaminomethoxybenzoyl tetrachlorobenzoate.**—When diethyl-*m*-aminophenol and tetrachlorophthalic acid anhydride condense, under such conditions that tetrachlororhodamine formation does not take place, the product resulting is made up of two molecules of the diethyl-*m*-aminophenol to one of the tetrachlorophthalic acid anhydride and not one molecule to one molecule as Haller and Umbgrove state (page 2103). The condensation was brought about, both in toluene according to the German patent 118077 (page 2103), and by heating a mixture of the two components as described by Haller and Umbgrove (page 2103). The following are the detailed experiments:

(a) One molecule of diethyl-*m*-aminophenol to one molecule of tetrachlorophthalic acid anhydride in toluene solution.

Twelve grams of diethyl-*m*-aminophenol were dissolved in toluene and a solution of 20 g. of tetrachlorophthalic acid anhydride in toluene added. When the two nearly colorless solutions were mixed, a red color developed. The solution was heated to boiling and after several hours a white precipitate began to settle from the boiling toluene. When this precipitate no longer increased in amount (which required about 20 hours) the boiling was stopped. The product consisting of white needles was filtered off and washed with methyl alcohol. Yield 17.9 g. corresponding to 80% of the calculated amount (figured from the diethyl-*m*-aminophenol). The filtrate evaporated to dryness left a residue of between 5 and 6 g., which was found to be mostly tetrachlorophthalic acid anhydride.

(b) Two molecules of diethyl-*m*-aminophenol to one molecule of tetrachlorophthalic acid anhydride in toluene solution.

The procedure was exactly the same as in (a) except that 18 g. of diethyl-*m*-aminophenol and 18 g. of tetrachlorophthalic acid anhydride

<sup>1</sup> International atomic weights (1916) are used in this paper.

<sup>2</sup> *Am. Chem. J.*, 41, 399 (1909).

were used. This allows for a slight excess of the anhydride. Yield 29.3 g. corresponding to 87% of the calculated amount.

(c) Fusion: one molecule of diethyl-*m*-aminophenol to one molecule of tetrachlorophthalic acid anhydride.

Twelve grams of diethyl-*m*-aminophenol and 20 g. of tetrachlorophthalic acid anhydride were fused in an atmosphere of carbon dioxide at 120° and at the same time the fused mass was stirred. After the melted mass became solid, it was crystallized once from toluene to remove any of the unchanged components. Yield 15 g. corresponding to 67% of the calculated amount.

(d) Fusion: two molecules of diethyl-*m*-aminophenol to one molecule of tetrachlorophthalic acid anhydride.

Thirty-six grams of diethyl-*m*-aminophenol and 36 g. of tetrachlorophthalic acid anhydride were fused as in (c). The melted mass thickened appreciably in ten minutes and was solid in half an hour. At first the temperature of the fused mass was about 30° to 45° higher than the temperature of the bath, but at the end of about 20 minutes it began to drop. During the fusion the contents of the flask *lost no weight*. The product, which had a bluish violet color, was crystallized once from toluene. Yield 65 g. corresponding to 96% of the calculated amount.

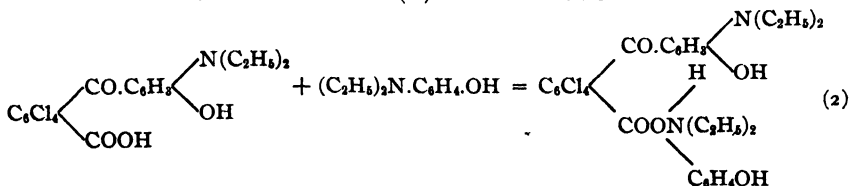
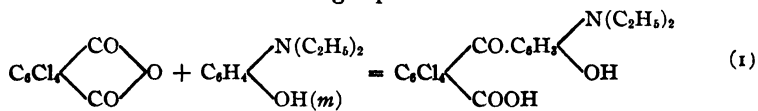
The condensation product crystallizes from methyl alcohol in prisms, containing no solvent of crystallization, which grind to a powder having a very faint yellowish tinge. It decomposes at 198° to a red liquid. When dried at 130° to constant weight, all products gave the same results on analysis.

Subst., *a*, 0.1610; *b*, 0.2873; *c*, 0.2280; *d*, 0.2768; cc. 0.1 *N* AgNO<sub>3</sub>, *a*, 10.45; *b*, 18.64; *c*, 14.76; *d*, 17.95.

Subst., *b*, 0.7282; *d*, 0.3345; cc. 0.1 *N* HCl, *b*, 23.68; *d*, 10.51.

Calc. for C<sub>23</sub>H<sub>30</sub>N<sub>2</sub>O<sub>5</sub>Cl<sub>4</sub>: Cl, 23.02; N, 4.55. Found: Cl, *a*, 23.02; *b*, 23.01; *c*, 22.96; *d*, 22.99; N, *b*, 4.56; *d*, 4.42.

It is therefore the result of the condensation of two molecules of diethyl-*m*-aminophenol with one molecule of tetrachlorophthalic acid anhydride as shown in the following equations:



Hydroxyphenyldiethylammoniumdiethylamino-*m*-hydroxybenzoyltetra-

chlorobenzoate is slightly soluble in benzene, more so in toluene and xylene. It is soluble in methyl and ethyl alcohols, glacial acetic acid, and acetone; insoluble in water. It dissolves in solutions of caustic alkalis, alkali carbonates and ammonium hydroxide with a yellow color which gradually darkens. After some time a bright yellow precipitate forms which was found to be a salt of an acid containing but three atoms of chlorine. This trichloro acid will be taken up in detail later (page 2111). The removal of one atom of chlorine takes place very quickly when the alkaline solutions are heated to their boiling points which was proven in the following way: A weighed quantity of the tetrachloro product was dissolved in 2.5% aqueous potassium hydroxide and the solution heated until the potassium salt of the trichloro acid had entirely separated. The solution was made strongly acid, with concentrated nitric acid and filtered. An excess of standard silver nitrate solution was added to the filtrate and the silver chloride removed. The silver nitrate in the filtrate was titrated with standard ammonium thiocyanate. The weight of chlorine equivalent to the volume of standard silver nitrate solution used up, gave the weight of chlorine removed from the tetrachloro product.

Subst., I, 0.6250; II, 0.7867; cc. 0.1 *N* AgNO<sub>3</sub>, I, 9.62; II, 12.18.

Calc. for one atom Cl, grams, I, 0.03594; II, 0.04524. Found: Cl, grams, I, 0.03414; II, 0.04318.

On account of the darkening of the alkaline solutions of the tetrachloro product, it was concluded that the second molecule of the diethyl-*m*-aminophenol is present in the form of a substituted ammonium radical and that the darkening is due to the fact that this second molecule is split off by the alkali and then the case is simply one of the increased sensitiveness of the alkylaminophenol in alkaline solution to the action of the oxygen of the air. If this is so, then concentrated mineral acids, as well as alkalis, should split off this second molecule of diethyl-*m*-aminophenol, and give the tetrachloro acid. This actually takes place under the influence of an alkali or a mineral acid.

(a) 24.8 g. of the original tetrachloro condensation product were dissolved in cold 5% aqueous sodium hydroxide and *immediately* poured into dilute sulfuric acid. A yellow product separated which weighed 17.8 g., corresponding to 99% of the calculated amount. It crystallized from methyl alcohol in the form of light yellow prisms, which decomposed at 217° forming a red liquid.

(b) Some of the original tetrachloro condensation product was dissolved in cold concentrated sulfuric acid, and the solution poured into distilled water kept cold by a freezing mixture. Reddish flakes separated. By crystallization from alcohol, a yellow product was finally obtained which decomposed at 217° forming a red liquid.

When dried to constant weight at  $130^{\circ}$ , analyses of both products proved them to be the tetrachloro acid.

Subst., I, 0.2156; II, 0.2500; cc. 0.1  $N$   $AgNO_3$ , I, 19.16; II, 22.27.

Subst., I, 0.4631; II, 0.5673; cc. 0.1  $N$   $HCl$ , I, 10.46; II, 13.17.

Calc. for  $C_{18}H_{18}O_4NCl_4$ : Cl, 31.45; N, 3.11. Found: Cl, I, 31.52; II, 31.59; N, I, 3.16; II, 3.25.

**Diethylamino-*m*-hydroxybenzoyltetrachlorobenzoic Acid.**—This acid crystallizes from methyl alcohol, ethyl alcohol, acetone and ether in pale yellow prisms containing no solvent of crystallization. It dissolves in solutions of the caustic alkalis, alkali carbonates and ammonium hydroxide with a yellow color *which does not darken on standing*. It is but slightly soluble in benzene and toluene; insoluble in water. That the tetrachloro acid loses an atom of chlorine when heated with caustic alkalis was proven in the same way as with the original condensation product (page 2107).

Subst., I, 0.6448; II, 0.7234; cc. 0.1  $N$   $AgNO_3$ , I, 13.91; II, 15.29.

Calc. for one atom Cl, grams, I, 0.05668; II, 0.05686. Found: Cl, grams, I, 0.04931; II, 0.05423.

In 10% solutions of the caustic alkalis there is no separation of the yellow colored salt of the trichloro acid until the solution is heated or diluted with water (page 2117).

**Action of Dry Ammonia Gas on the Tetrachloro Acid.**—A weighed quantity of the acid, dried at  $130^{\circ}$ , was treated with dry ammonia gas. It absorbed ammonia very rapidly at first, becoming slightly brighter yellow in color, and at the end of 24 hours had reached constant weight, showing an increase corresponding to two molecules of ammonia.

Subst., 0.6477; gain,  $NH_3$ , 0.0507.

Calc. for  $C_{18}H_{18}O_4NCl_4(NH_3)_2$ :  $NH_3$ , 7.02. Found:  $NH_3$ , 7.26.

When a current of dry air is passed over this diammonium salt it loses one molecule of its ammonia and becomes constant in weight. The mono-ammonium salt is hygroscopic.

**Silver Salt of the Tetrachloro Acid.**—Five grams of the tetrachloro acid were dissolved in absolute alcohol and 70 cc. of an alcoholic solution of silver nitrate (32 g. to the liter) added. After some time the silver salt precipitated in the form of yellow crystals. These were analyzed for silver as follows: A weighed amount was dissolved in concentrated nitric acid, poured into distilled water, the tetrachloro acid filtered off and the silver determined by titrating with standard ammonium thiocyanate solution.

Subst., I, 0.7612; II, 0.6391; cc. 0.1  $N$   $NH_4SCN$ , I, 13.66; II, 11.43.

Calc. for  $C_{18}H_{18}O_4NCl_4Ag$ : Ag, 19.34. Found: Ag, I, 19.36; II, 19.29.

**Methyl Ester of the Tetrachloro Acid.**—Fifteen grams of the tetrachloro acid were heated to boiling for 9 hours with 300 cc. of a 3% solu-

tion of dry hydrochloric acid gas in absolute methyl alcohol. On cooling, the solution was poured into its own volume of water. The ester separated as an amorphous body, which gradually became granular. It was purified by crystallization from ether. The ester has a very faint yellow color and melts at 146–148° to a clear yellow liquid. As the substance on being heated to even 100°, showed signs of decomposition, the analyses were made on the air-dried material.

Subst., I, 0.2267; II, 0.2142; cc. 0.1 *N* AgNO<sub>3</sub>, I, 19.56; II, 18.47.

Calc. for C<sub>18</sub>H<sub>14</sub>NO<sub>4</sub>Cl<sub>4</sub>CH<sub>3</sub>: Cl, 30.50. Found: Cl, I, 30.60; II, 30.57.

The methyl ester shows an extraordinary solubility, being soluble in methyl alcohol, ethyl alcohol, ether, benzene, toluene, chloroform, carbon tetrachloride, acetone and ethyl acetate.

**Ethyl Ester of the Tetrachloro Acid.**—The preparation was exactly analogous to that of the methyl ester, using a 3% solution of dry hydrochloric acid gas in ethyl alcohol. The ethyl ester was purified by crystallization from ether and is very like the methyl ester in its appearance and solubilities. It melts at 120° to a clear yellow liquid. Analyses of the air-dried material gave the following results:

Subst., I, 0.1992; II, 0.2125; cc. 0.1 *N* AgNO<sub>3</sub>, I, 16.66; II, 17.83.

Calc. for C<sub>18</sub>H<sub>14</sub>NO<sub>4</sub>Cl<sub>4</sub>C<sub>2</sub>H<sub>5</sub>: Cl, 29.61. Found: Cl, I, 29.65; II, 29.75.

**Acetylation Products of the Tetrachloro Acid.**—Ten grams of the tetrachloro acid were heated with 70 g. of acetic anhydride for 7 hours on a boiling water bath. Previous experiments had shown that two products were formed, one of which is changed by boiling with alcohols. With this in mind, part of the solution was poured into a well cooled mixture of equal parts of acetone and water and the whole vigorously shaken. The acetylation products separated as a yellowish brown precipitate. This was dissolved in acetone and precipitated by the addition of water. This procedure was repeated until the substance was obtained free from the odor of acetic anhydride. It was dissolved in ether, the solution boiled for 10 minutes with boneblack and filtered, giving a bright yellow solution. From this, after repeated fractional crystallization, there was obtained a small quantity of a white product melting at 230–231°, and which analyses showed to be a diacetate of the tetrachloro acid.

Subst., I, 0.1585; II, 0.1643; cc. 0.1 *N* AgNO<sub>3</sub>, I, 11.86; II, 12.26.

Calc. for C<sub>18</sub>H<sub>12</sub>NO<sub>4</sub>Cl<sub>4</sub>(COCH<sub>3</sub>)<sub>2</sub>: Cl, 26.51. Found: Cl, I, 26.53; II, 26.47.

There was also obtained a much larger amount of a pale yellow product, melting at 174–180° and which was also a diacetate of the tetrachloro acid.

Subst., I, 0.2143; II, 0.2780; cc. 0.1 *N* AgNO<sub>3</sub>, I, 16.03; II, 20.79.

Calc. for C<sub>18</sub>H<sub>12</sub>NO<sub>4</sub>Cl<sub>4</sub>(COCH<sub>3</sub>)<sub>2</sub>: Cl, 26.51. Found: Cl, I, 26.52; II, 26.52.

**Methyl and Ethyl Esters of the Monoacetate of the Tetrachloro Acid.**—

The remainder of the acetic anhydride solution was poured into absolute ethyl alcohol. Grayish white crystals separated on standing, which on

crystallization from ether, gave a pale yellow product which melted at  $174-180^{\circ}$  and was identical with the yellow diacetate. The filtrate was boiled to convert the acetic anhydride into ethyl acetate and from this solution, after repeated fractional crystallization, two substances were obtained, one, a white product in very small amount, melting at  $230-231^{\circ}$ , identical with the white diacetate; the other in larger amount, a yellow substance, melting at  $190-192^{\circ}$ , and which analyses showed to be the ethyl ester of the monoacetate of the tetrachloro acid.

Subst., I, 0.1999; II, 0.1872; cc. 0.1  $N$   $AgNO_3$ , I, 15.42; II, 14.41.

Calc. for  $C_{18}H_{13}NO_4Cl_4(COCH_3)(C_2H_5)$ : Cl, 27.22. Found: Cl, I, 27.35; II, 27.29. Two portions of the pale yellow product, melting at  $174-180^{\circ}$ , were boiled for 6 hours, one with ethyl alcohol and the other with methyl alcohol. From the ethyl alcohol solution, a yellow product was obtained melting at  $190-192^{\circ}$  and identical with the ethyl ester of the monoacetate. The methyl alcohol solution gave a yellow product melting at  $152-155^{\circ}$  and which analyses showed to be the methyl ester of the monoacetate of the tetrachloro acid.

Subst., I, 0.1888; II, 0.1940; cc. 0.1  $N$   $AgNO_3$ , I, 14.90; II, 15.32.

Calc. for  $C_{18}H_{13}NO_4Cl_4(COCH_3)(CH_3)$ : Cl, 27.98. Found: Cl, I, 27.98; II, 28.00.

The pale yellow product melting at  $174-180^{\circ}$  is therefore an acetate of a mixed anhydride similar to the one obtained by Haller and Umbgrove (page 2102). The white product melting at  $230-231^{\circ}$  undergoes no change when boiled with alcohols and is undoubtedly a true diacetate of the tetrachloro acid (page 2116).

Both the white and yellow acetylation products gradually dissolve in 2% aqueous potassium hydroxide solution. This shows that they are gradually saponified and go into solution as the yellow potassium salt of the tetrachloro acid. On longer standing, an atom of chlorine is removed, and the salt of the trichloro acid (page 2111) precipitates.

Both of the acetylation products are readily soluble in methyl alcohol, ethyl alcohol, benzene, chloroform, carbon tetrachloride, acetone, ethyl acetate and ether.

**Action of Dry Hydrochloric Acid Gas on the Tetrachloro Acid.**—A known weight of the dry tetrachloro acid was treated with dry hydrochloric acid gas. It rapidly increased in weight becoming constant at the end of 3 hours and absorbing an amount of hydrochloric acid corresponding to slightly more than one molecule when it was colorless.

Subst. 0.3308; gain, HCl, 0.0280.

Calc. for  $C_{18}H_{13}O_4NCl_4.HCl$ : HCl, 7.48. Found: HCl, 7.80.

When exposed to dry air it quickly loses most of its hydrochloric acid, finally returning to its original weight in about 20 hours. When the excess of hydrochloric acid over one molecule is lost, the substance changes to a light yellow.

**Action of Dry Hydrochloric Acid Gas on the Methyl Ester of the Tetrachloro Acid.**—When this compound is treated with dry hydrochloric acid gas, it rapidly takes up two molecules and the dihydrochloride formed is colorless.

Subst., 0.3458; gain, HCl, 0.0542.

Calc. for  $C_{19}H_{17}O_4NCl_4 \cdot 2HCl$ : HCl, 13.56. Found: HCl, 13.55.

When this is placed in dry air it quickly loses one molecule of hydrochloric acid and changes to a pale yellow. The second molecule of hydrochloric acid is lost very slowly, in fact at the end of 14 days the substance still retained nearly 3% of hydrochloric acid.

**Action of Dry Hydrochloric Acid Gas on the Methyl Ester of the Monoacetate of the Tetrachloro Acid.**—When this substance is placed in dry hydrochloric acid gas, it quickly takes up more than two molecules and becomes colorless.

Subst., 0.2802; gain, HCl, 0.0439.

Calc. for  $C_{21}H_{19}NO_3Cl_4 \cdot 2HCl$ : HCl, 12.27. Found: HCl, 13.54.

The dihydrochloride in dry air gradually loses weight and becomes constant, holding one molecule of hydrochloric acid at room temperature. The monohydrochloride is light yellow in color.

**Potassium Salt of the Trichloro Acid.**—This salt was prepared by dissolving the tetrachloro acid in aqueous 3% potassium hydroxide and heating the solution to boiling by passing in steam, when the yellow potassium salt of the trichloro acid separated. It crystallizes from methyl alcohol in bright yellow needles which melt at  $285^\circ$  to a pale red liquid. When crystallized from ethyl alcohol it had the same melting point. The crystals, from both methyl alcohol (I) and ethyl alcohol (II) contain two molecules of water of crystallization. This was shown by making potassium determinations on the air-dried product from the two solvents and also by determining the loss in weight on heating. A weighed quantity of the salt was dissolved in boiling water, an excess of standard hydrochloric acid added, the trichloro acid filtered off and the excess of hydrochloric acid titrated with standard sodium hydroxide solution.

Subst., I, 0.8536; II, 0.5652; cc. 0.1 *N* HCl, I, 17.36; II, 11.95.

Calc. for  $C_{18}H_{13}NO_4Cl_3K \cdot 2H_2O$ : K, 8.00. Found: K, I, 7.95; II, 8.27.

Loss in weight at  $160^\circ$ :

Subst., I, 0.4433; II, 0.5278; loss, I, 0.0374; II, 0.0422.

Calc. for  $C_{18}H_{13}NO_4Cl_3K \cdot 2H_2O$ :  $H_2O$ , 7.37. Found:  $H_2O$ , I, 8.44; II, 8.00.

Drops of water collected on the cool end of the drying tube in both determinations.

The dried product was analyzed for chlorine, nitrogen, and potassium.

Subst., I, 0.2967; II, 0.2434; cc. 0.1 *N*  $AgNO_3$ , I, 19.75; II, 10.18.

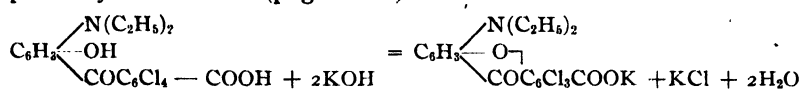
Subst., I, 0.4926; II, 0.5872; cc. 0.1 *N* HCl, I, 11.21; II, 12.83.

Subst., I, 0.5468; II, 0.6321; cc. 0.1 *N* HCl, I, 12.17; II, 14.03.

Calc. for  $C_{18}H_{13}NO_4Cl_3K$ : Cl, 23.51; N, 3.10; K, 8.64. Found: Cl, I, 23.60; II, 23.57; N, I, 3.19; II, 3.06; K, I, 8.70; II, 8.68.

As it has already been shown that one atom of chlorine is removed from

the tetrachloro acid by the potassium hydroxide (page 2108), the reaction is probably as follows (page 2118):



This potassium salt is soluble in methyl alcohol, ethyl alcohol, glacial acetic acid; slightly soluble in acetone, benzene and ether. It is quite soluble in hot water, from which it is precipitated by a solution of potassium hydroxide. This product loses weight when heated to 160° corresponding to three molecules of water of crystallization.

Subst., 0.9203; loss, H<sub>2</sub>O, 0.1017.

Calc. for C<sub>18</sub>H<sub>13</sub>NO<sub>4</sub>Cl<sub>3</sub>K·3H<sub>2</sub>O: H<sub>2</sub>O, 10.67. Found: H<sub>2</sub>O, 11.05.

**Trichlorodiethylaminioxanthonecarboxylic Acid.**—This compound was made by dissolving the potassium salt described above in boiling water, and adding hydrochloric acid to the solution. The trichloro acid separates as an amorphous mass. It crystallizes from methyl alcohol in bright yellow needles which melt at 278° to a pale red liquid. It also crystallizes from ethyl alcohol in bright yellow needles melting at 278°, but which contain *no solvent of crystallization*. The product from methyl alcohol, when heated to 160°, rapidly comes to constant weight, no moisture collects on the cool end of the drying tube and the loss is equivalent to exactly one molecule of methyl alcohol.

Subst., 1.1912; loss, CH<sub>3</sub>OH, 0.0857.

Calc. for C<sub>18</sub>H<sub>11</sub>NO<sub>4</sub>Cl<sub>3</sub>·CH<sub>3</sub>OH: CH<sub>3</sub>OH, 7.19. Found: CH<sub>3</sub>OH, 7.17.

The residue when analyzed for chlorine and nitrogen proved to be the trichloro acid (page 2118).

Subst., I, 0.2006; II, 0.2370; cc. 0.1 N AgNO<sub>3</sub>, I, 14.51; II, 17.16.

Subst., I, 0.6437; II, 0.7126; cc. 0.1 N HCl, I, 15.80; II, 16.94.

Calc. for C<sub>18</sub>H<sub>11</sub>NO<sub>4</sub>Cl<sub>3</sub>: Cl, 25.66; N, 3.38. Found: Cl, I, 25.65; II, 25.68; N, I, 3.44; II, 3.33.

To determine whether the acid is precipitated from a solution of its potassium salt as the trichloro acid or as a hydrate of this acid (page 2118) some of the powdered salt was suspended in cold water, concentrated hydrochloric acid added and the mixture thoroughly shaken to coagulate the trichloro acid set free. This was filtered off and washed with water until free from hydrochloric acid. At the same time, some of the potassium salt was dissolved in boiling water and the trichloro acid precipitated from this solution by the addition of concentrated hydrochloric acid. Moisture determinations were made on the two air-dried products:

Subst., I, 0.4151; II, 0.3867; loss, H<sub>2</sub>O, I, 0.0104; II, 0.0176.

Calc. for C<sub>18</sub>H<sub>11</sub>NO<sub>4</sub>Cl<sub>3</sub>·H<sub>2</sub>O: H<sub>2</sub>O, 4.16. Found: H<sub>2</sub>O, I, 2.50; II, 4.55.

(I) was made on the trichloro acid precipitated from the boiling solution, while (II) was made on the acid precipitated cold. The heating was begun at 115° and at the end of each hour the material was weighed,



returned to the drying tube and the temperature increased until the final heating was at  $175^{\circ}$ . In (I), the substance lost no weight after heating for one hour at  $115^{\circ}$ , while in the other case it was heated for one and one-half hours at  $115^{\circ}$  and one hour at  $140^{\circ}$  before it reached constant weight. In neither case did any moisture collect on the cool end of the drying tube. These results show that the acid precipitated in the cold from its potassium salt is obtained as the hydrate (page 2118), which readily loses a molecule of water of constitution and that it loses part of this water when precipitated out of a boiling solution of the salt with acids.

The trichloro acid is soluble in methyl alcohol, ethyl alcohol and glacial acetic acid, less soluble in acetone; insoluble in water. It is very stable toward alkalis, no chlorine being removed even when it is boiled with alcoholic caustic potash. It is highly probable that the yellow product obtained by Bloch (page 2104) is the trichloro*dimethylaminoxanthone*-carboxylic acid.

**Action of Dry Ammonia Gas on the Dried Trichloro Acid.**—When a weighed quantity of the trichloro acid, dried at  $160^{\circ}$ , is treated with dry ammonia gas it rapidly absorbs more than one molecule of ammonia with no noticeable change of color.

Subst., 0.7068; gain,  $\text{NH}_3$ , 0.0406.

Calc. for  $\text{C}_{18}\text{H}_{14}\text{NO}_4\text{Cl}_3\cdot\text{NH}_3$ :  $\text{NH}_3$ , 3.95. Found:  $\text{NH}_3$ , 5.43.

This compound, when exposed to dry air, loses its excess of ammonia over one molecule very rapidly. The monoammonium salt left is hygroscopic but stable.

**Action of Acetic Anhydride on the Trichloro Acid.** Ten grams of the trichloro acid were boiled for 3 hours with 70 g. of acetic anhydride. On cooling, a product separated which was filtered off, washed with cold absolute alcohol and air-dried. It crystallizes in bright yellow needles, melts at  $188\text{--}190^{\circ}$ , with slight decomposition and on drying at  $120^{\circ}$ , loses no appreciable weight. Analyses on the dried product gave the following results:

Subst., I, 0.1902; II, 0.1686; cc. 0.1  $\text{N}$   $\text{AgNO}_3$ , I, 12.52; II, 11.12.

Calc. for  $\text{C}_{18}\text{H}_{12}\text{NO}_4\text{Cl}_3(\text{COCH}_3)$ : Cl, 23.30. Found: Cl, I, 23.34; II, 23.39.

The yellow acetate is soluble in acetic anhydride, methyl alcohol, ethyl alcohol, acetone and benzene; insoluble in water. When crystallized from acetone, a yellow powder is obtained which melts very indefinitely at about  $185^{\circ}$ . This was heated at  $155\text{--}160^{\circ}$  for 25 hours before it reached constant weight and showed a loss of 11.20%. A current of dry air was passed over the compound while it was being heated and on leaving the drying tube this current of air was led through a gas wash bottle containing distilled water. After the compound had reached constant weight, the water in this wash bottle gave a strong iodoform

test for acetone. The product after heating melts at  $278^{\circ}$ , the melting point of the trichloro acid.

Subst., 0.5428; loss, acetone, 0.0608.

Calc. for  $C_{18}H_{14}NO_4Cl_3(C_3H_5O)$ : acetone, 12.28. Found: acetone, 11.20.

Hence, the acetate when crystallized from acetone forms an acetate of the trichloro acid (page 2119).

A portion of the yellow acetate was boiled with ethyl alcohol for six hours and the solution cooled. A product separated in the form of bright yellow needles, melting at  $278^{\circ}$ , the melting point of the trichloro acid. On drying at  $160^{\circ}$ , this material lost no weight.

The product obtained by the action of acetic anhydride on the trichloro acid is therefore a mixed anhydride rather than a true acetate (pages 2102, 2118).

Attempts to make the methyl ester of the trichloro acid by the catalytic method of esterification resulted in failure. This is in accord with the fact that the acetyl group is removed from the mixed anhydride when it is boiled with ethyl alcohol but the product formed is the free acid and not the ester.

#### **Action of Dry Hydrochloric Acid Gas on the Dry Trichloro Acid.—**

A weighed amount of dry trichloro acid was treated with dry hydrochloric acid gas. At the end of three hours it showed no change in appearance and had absorbed only 0.3% of hydrochloric acid. When concentrated hydrochloric acid is added to the trichloro acid, it does not go into solution, but turns white. This white hydrochloride when filtered off and dried in the air loses hydrochloric acid as it dries, and turns yellow.

**Action of Dry Hydrochloric Acid Gas on the Mixed Anhydride of the Trichloro Acid and Acetic Acid.**—The mixed anhydride dried at  $120^{\circ}$  absorbs one molecule of hydrochloric acid gas in two hours and has a pale yellow color. At the end of six hours it reaches constant weight, having absorbed more than one molecule and is colorless.

Subst., 0.4016; gain, HCl, 0.0414.

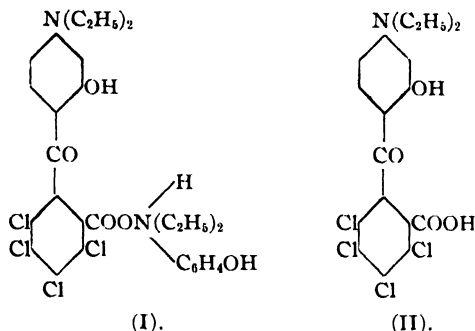
Calc. for  $C_{20}H_{16}NO_5Cl_3.HCl$ : HCl, 7.40. Found: HCl, 9.35.

The hydrochloride loses all its hydrochloric acid on standing over night at room temperature in dry air.

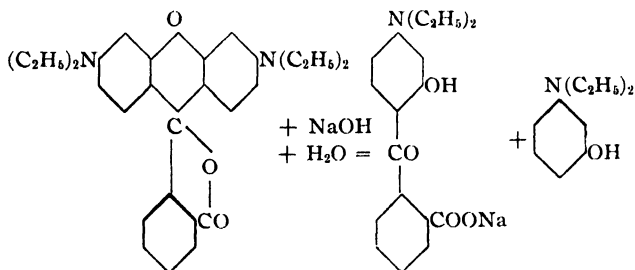
#### **Theoretical.**

Hydroxyphenyldiethylammonium - diethylamino - *m* - hydroxybenzoyl-tetra-chlorobenzoate is the product resulting from the condensation of diethyl-*m*-aminophenol and tetrachlorophthalic acid anhydride under such conditions that tetrachlororhodamine formation does not take place. It seems highly probable that the reaction proceeds in two stages (page 2106), and that the tetrachloro acid is first formed. However, the *final product* is always the substituted ammonium salt of the tetrachloro

acid, whether the condensation is brought about in toluene solution or by direct heating of the two components.



Formula (I) for this salt explains the readiness with which it is decomposed into the tetrachloro acid, (II) and diethyl-*m*-aminophenol by the action of alkalis and mineral acids and also the color of the compound. That the ketone group occupies the *ortho* position to the hydroxyl, follows from the ease with which the tetrachloro acid is converted into the trichloro acid by weak alkalis (page 2111) and also from the color of the compound, Staedel<sup>1</sup> having shown that the *ortho*hydroxybenzophenones are yellow. That the diethylamino group is in the *para* position is proved by the fact that the tetrachloro acid is so readily converted into tetrachlororhodamine.<sup>2</sup> The decomposition of tetraethylrhodamine into *p*-diethylamino-*m*-hydroxybenzoyl-*o*-benzoic acid (page 2102) and diethyl-*m*-aminophenol:



is also in accord with the above view of the structure of the tetrachloro acid.

Like the phthaleins, the tetrachloro acid yields derivatives of a tautomeric form such as the diacetate and the free acid may be a mixture of this form (II) with the ketone form (I) (page 2116).

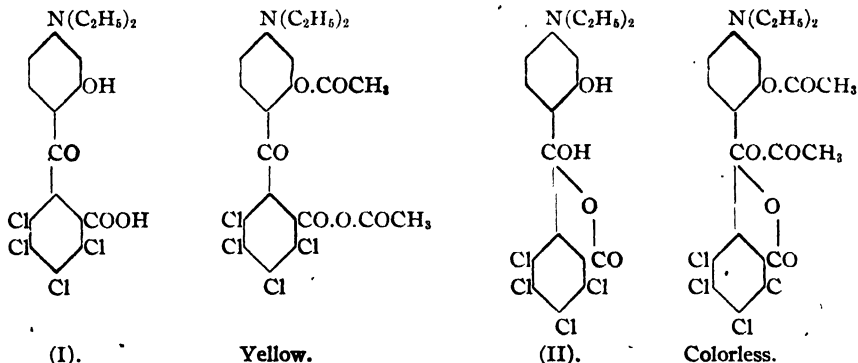
When the tetrachloro acid is treated with dry ammonia, it first forms the true ammonium salt, and then absorbs a second molecule of ammonia

<sup>1</sup> *Ann.*, **283**, 175 (1894).

<sup>2</sup> *Bull. soc. chim.*, **25**, 747 (1901).

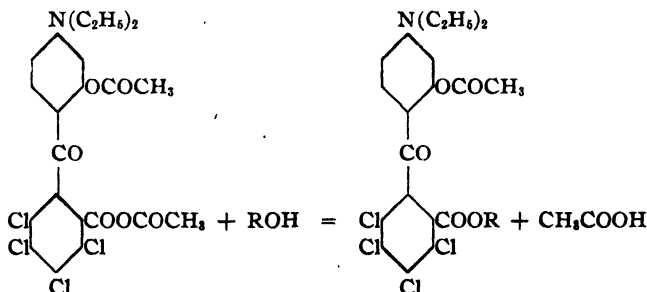
to neutralize the phenol hydroxyl group. This diammonium salt loses the molecule of ammonia absorbed by the hydroxyl group very readily in dry air at room temperature giving a stable monoammonium salt. This behavior is evidence of the strong acid character of the molecule. The fact that the tetrachloro acid forms esters so readily by the catalytic method of esterification, unlike the tetrachloro acid of Haller and Umbgrove (page 2102), is worthy of note, since it forms an exception to the Victor Meyer rule.

The behavior of the tetrachloro acid with acetic anhydride shows that it acts as a tautomeric substance.



The yellow product, melting at  $174-180^\circ$  is a derivative of Formula (I), while the colorless product melting at  $230-231^\circ$  is a derivative of Formula (II).

That the yellow product has the formula assigned to it is confirmed by its forming esters of the monoacetate when boiled with alcohols according to the equation

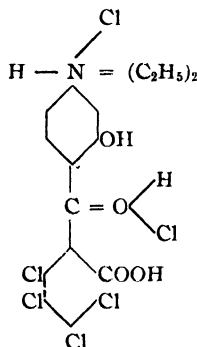


It is not then a true diacetate of the tetrachloro acid, but the monoacetate of the mixed anhydride of the tetrachloro acid and acetic acid as shown above.

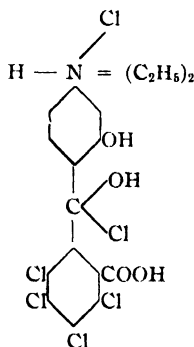
Its color is probably due to the ketone group connected with the two benzene residues as in the case of the tetrachloro acid. The white product

is a true diacetate of the tetrachloro acid, as it is not changed by boiling with alcohols and has no color. The absence of color is due to the fact that the ketone group is no longer present.

The behavior of the tetrachloro acid toward dry hydrochloric gas shows its basic nature. It absorbs more than one molecule, but loses the excess quite readily in dry air at room temperature. The monohydrochloride is yellow while the salt containing an excess of hydrochloric acid is colorless. The excess of hydrochloric acid may be absorbed by the ketone group, forming an oxonium salt or a carbonium salt.



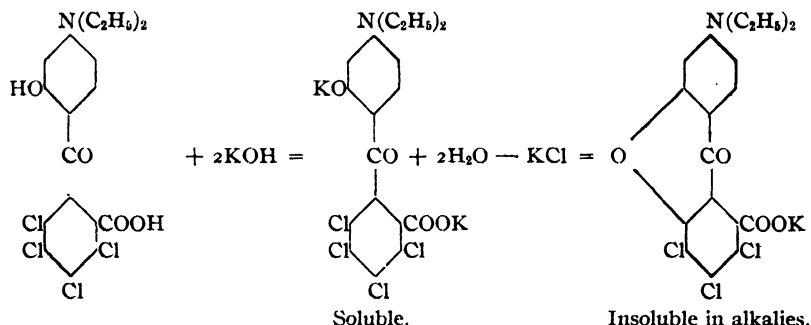
Oxonium salt.



Carbonium salt.

Both formulas show why the salt having an excess of hydrochloric acid is colorless, as both in the oxonium salt and in the carbonium salt the ketone group is no longer present. The hydrochloric acid absorbed by the ketone group is the first to be lost in dry air and the yellow color returns. When the acid group is neutralized by a methyl or ethyl radical, the ester forms a dihydrochloride which is colorless for the same reason that the tetrachloro acid containing an excess of hydrochloric acid is colorless. It is not until the phenol hydroxyl group as well as the carboxyl group is neutralized that a hydrochloride stable at room temperature is formed. The methyl ester of the monoacetate of the tetrachloro acid absorbs two molecules of hydrochloric acid and the dihydrochloride is colorless. It loses one molecule of its hydrochloric acid at room temperature and the monohydrochloride is yellow and stable.

The removal of chlorine from the tetrachloro acid by even such weak alkaline solutions as ammonium hydroxide and sodium carbonate is of special interest as it is the first case of its kind to be noticed in this laboratory where the tetrachloro compounds have received considerable attention. As the alkali salts do not precipitate from 10% solutions of the caustic alkalis until the solutions are diluted or heated, it is very probable that the reaction in which the chlorine is removed takes place in stages as follows:

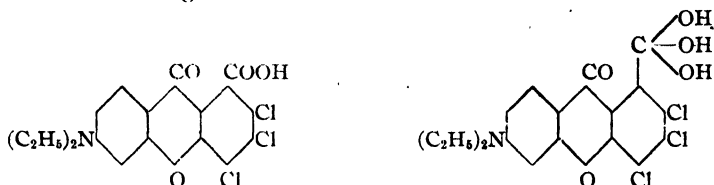


The fact that the salt of the trichloro acid and the acid itself are much more *highly colored* than the corresponding tetrachloro compounds is also in accord with this view, as ring formation is frequently attended with an increase of color.

The free trichloro acid is readily obtained by decomposing its salts with mineral acids. It is precipitated from its potassium salt in the cold as a hydrate (page 2112), while from a boiling solution it is obtained nearly anhydrous.

It is rather curious that it should crystallize from methyl alcohol with a molecule of methyl alcohol, while it crystallizes from ethyl alcohol with no solvent of crystallization. This is probably due to the fact that methyl alcohol is more nearly like water in its properties than is ethyl alcohol.

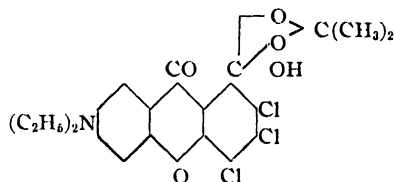
The trichloro acid and its hydrate are hence derivatives of xanthone and have the following structures:



The name of the acid is, therefore, 2,3,4-trichloro-6-diethylamino-xanthone-1-carboxylic acid.

Like the tetrachloro acid, the trichloro acid combines with dry ammonia to form a monoammonium salt which is stable at room temperature.

There being no hydroxyl groups present in the molecule, the trichloro acid reacts with acetic anhydride to form a mixed anhydride (page 2113) as in the case of the acid obtained by Haller and Umbgrove (page 2102). This mixed anhydride is very unstable as is shown by the fact that the acetyl group is removed by boiling with ethyl alcohol and the acid is set free instead of ester formation taking place. The acetate of the trichloro acid formed when the mixed anhydride is boiled with acetone probably has the following structure:



The fact that the trichloro acid does not form a methyl ester by the catalytic method of esterification is probably due to steric hindrance.

The trichloro acid does not absorb hydrochloric acid gas as the diethylamino group is here neutralized by the carboxyl group. When the hydrogen atom of this carboxyl group is replaced by an acetyl group the mixed anhydride absorbs more than one molecule of hydrochloric acid and is colorless. The excess of hydrochloric acid is probably taken up in this case by the ketone group forming an oxonium or a carbonium salt as in the case of the hydrochlorides of the tetrachloro compounds.

### Summary.

The results of this investigation may be briefly stated as follows:

1. The condensation of diethyl-*m*-aminophenol and tetrachlorophthalic acid anhydride has been effected in both an indifferent solution medium and by the direct heating of a mixture of the two components. The result of the condensation is always hydroxyphenyldiethylammonium-diethylamino-*m*-hydroxybenzoyl-tetrachlorobenzoate.
2. The tetrachloro acid has been prepared by decomposing the substituted ammonium salt first formed with mineral acids or alkalies.
3. The ammonium and silver salts, the methyl and ethyl esters, the acetate of the mixed anhydride of the tetrachloro acid and acetic acid, and the methyl and ethyl esters of the monoacetate of the tetrachloro acid have been prepared. All these compounds are colored and are derivatives of the keto-form of the tetrachloro acid.
4. A white diacetate has been prepared. This is a derivative of the tautomeric lactoid form of the tetrachloro acid.
5. The action of dry hydrochloric acid gas on the tetrachloro acid, its methyl ester and the methyl ester of its monoacetate has been studied.
6. One atom of chlorine has been removed from the tetrachloro acid together with an atom of hydrogen and the resulting trichloro acid, a xanthone derivative, has been obtained and studied.
7. The potassium and ammonium salts of the trichloro acid, the acetate of the trichloro acid and the mixed anhydride of the trichloro acid and acetic acid have been prepared.
8. The action of dry hydrochloric acid gas on the trichloro acid and on the mixed anhydride of the trichloro acid and acetic acid, has been studied.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY.]

**STUDIES IN THE PREPARATION OF NITRILES. II. THE PREPARATION OF ALIPHATIC NITRILES.**

BY G. D. VAN EPPS AND E. EMMET REID.

Received August 2, 1916

**Introduction.**

For the preparation of nitriles we have had the old method of Letts<sup>1</sup> as improved by Krüss,<sup>2</sup> which was to heat an acid, such as benzoic acid, with lead thiocyanate. This method was easy to carry out and gave fair yields. Several years ago,<sup>3</sup> in this laboratory, this method was studied and it was found that far better yields could be obtained by substituting the zinc salt of the acid for the free acid, but only aromatic acids were experimented with. The present work was taken up to test the applicability of this improved method to aliphatic nitriles and to find the best conditions for their preparation.

The preparation of acetonitrile has been studied most extensively on account of the importance and the availability of acetic acid. Various methods of heating have been experimented with. Zinc salts of acetic, propionic, butyric, isovaleric, stearic, phenylacetic, phenylpropionic, cinnamic, and terephthalic acids, and the lead salts of some of these acids, have been heated with lead thiocyanate. Several other thiocyanates have been used and the results compared with those obtained with the lead salt. Calcium, copper, stannous, manganous, nickel, cobalt, magnesium, strontium, barium and basic ferric acetates have been tried.

**Historical.**

E. A. Letts<sup>4</sup> of London, in 1872, studied the action of potassium thiocyanate on acids. In case of acetic acid, he could not obtain the nitrile, but with isobutyric acid and valeric acid he found both amide and nitrile, the amide being the main product. With benzoic acid the nitrile was almost the sole product, only traces of the amide being found.

Pfankuch<sup>5</sup> heated barium benzoate with excess of barium thiocyanate and got benzonitrile but mixed with large quantities of other products. Barium acetate and barium thiocyanate gave similar results, the other products being in excess of the acetonitrile.

Kekulé<sup>6</sup> reviewed the work up to his time and speculated as to the mechanism of the reaction, but made no advance in its application.

G. Krüss<sup>7</sup> complained of the yield in Letts' process and improved the

<sup>1</sup> *Ber.*, **5**, 669 (1872).

<sup>2</sup> *Ibid.*, **17**, 1766 (1884).

<sup>3</sup> *Am. Chem. J.*, **43**, 152 (1910).

<sup>4</sup> *Ber.*, **5**, 669 (1872).

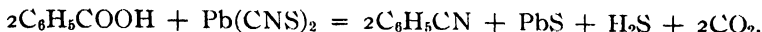
<sup>5</sup> *J. prakt. Chem.*, [2] **6**, 97 (1873).

<sup>6</sup> *Ber.*, **6**, 111 (1873).

<sup>7</sup> *Ibid.*, **17**, 1766 (1884).



method by substituting lead thiocyanate for the potassium salt. Krüss gives the equation



He reported a yield of 60 to 55 g. of benzonitrile from 100 g. of benzoic acid, or double what he was able to obtain by the method of Letts.

Reid<sup>1</sup> studied this reaction quantitatively and showed that it is not represented correctly by the equation given. He concluded that the nitrile is formed by interaction between the lead thiocyanate and the lead salt of the organic acid, this salt being formed by reaction between the free acid put in and a part of the lead thiocyanate. This led to a substitution of the previously prepared salt of the organic acid for the free acid, and to extended experiments with different salts, the conclusion being that the best yield is obtained when the zinc salt of the organic acid is used. Reid's method left little to be desired in the preparation of benzonitrile and other aromatic nitriles, both as to yield and convenience of work, but was not extended to aliphatic.

**Materials.**—*Lead thiocyanate* was prepared by precipitation from lead nitrate and ammonium thiocyanate. The precipitated salt was well washed with water, and twice with alcohol. The air-dried salt was further dried in an air-bath at 120°. The salt is pure white but turns somewhat yellow on long keeping. It blackens somewhat when dried in the air-bath.

*Zinc thiocyanate* was prepared by boiling ammonium thiocyanate with excess of zinc hydroxide till no more ammonia came off. The solution was filtered hot and evaporated to crystallization. The crystals were centrifuged. It is difficult to dry this salt as it fuses easily and begins to decompose at low temperatures. The salt is somewhat hygroscopic.

*Cuprous thiocyanate* was prepared by mixing copper sulfate and ammonium thiocyanate in the presence of sulfur dioxide. The gray salt was well washed with water and dried in an air-bath. It turns yellow.

*Zinc acetate, calcium acetate, zinc butyrate, zinc propionate, and zinc isovalerate* were prepared by boiling water solutions of the acids with excess of the carbonate of the metal. The solutions were filtered hot and evaporated to crystallization. The latter three salts were dried over sulfuric acid in a vacuum, the others were dried in an air-bath.

*Zinc stearate, lead phenylacetate, zinc phenylacetate, lead cinnamate, zinc cinnamate, zinc hydrocinnamate, lead benzoate, and zinc terephthalate* were prepared by double decomposition from the neutral ammonium or sodium salts of the acids and lead nitrate or zinc sulfate. All of these salts were dried in air-bath at 120°.

*Potassium thiocyanate, lead acetate, copper acetate, barium acetate, basic*

<sup>1</sup> *Am. Chem. J.*, **43**, 162 (1910).

*ferric acetate, stannous acetate, manganous acetate, nickel acetate, cobalt acetate, magnesium acetate, and strontium acetate* were good commercial preparations.

**Method of Work.**—In each experiment the salts were thoroughly dried and powdered. The weighed amounts were thoroughly mixed before the heating was begun. As the heat is applied the mixtures melt and blacken and bubbles of gas and vapors come from the pasty mass. Usually the nitrile begins to drop from the retort neck in a very short time. The reaction proceeds regularly and spreads through the whole mass, which becomes more or less liquid throughout. At the end of the reaction, the nitrile ceases to come off and the residue sets to a hard mass of the sulfides of the metals.

Five methods of heating the mixtures were tried. In the tables the experiments are marked with the letters, *a*, *b*, *c*, *d*, and *e* to show in which of these ways the operation was carried out.

*a.* Heating in an iron retort under reduced pressure. The retort used was such as is sold for the distillation of mercury and was of 500 cc. capacity. The lid was luted on with a ring of asbestos paper wet with glycerine. Reduced pressure was maintained by a water pump. The heating was so regulated that the pressure was kept 50 to 100 mm.

*b.* Heating in the iron retort under atmospheric pressure. In this the same retort was used. In both cases the retort was heated by a ring burner which supplied the heat uniformly to the walls of the retort, additional heat being supplied by a Bunsen burner to complete the reaction. The distillates from the iron retort were somewhat more colored than those from glass, owing to small amounts of iron dissolved.

*c.* Heating in a glass retort. The retorts used were of 250 and 500 cc. capacity without tubulature. The heating was done by means of a Bunsen burner held in the hand, and the heat was applied at first one spot and then another on the side and finally at the bottom. The retort may be cleaned with nitric acid and used repeatedly. With the glass retort, the course of the reaction is readily followed and it is readily kept under control.

*d.* Heating in a horizontal glass tube. The tube used was of hard glass, 175 mm. long and 22 mm. in diameter, and closed at one end. The open end was closed by a cork through which a narrower tube passed to the condenser. The heating was done by a burner held in the hand. This was used for small scale experiments. It has the advantage that the nitrile does not condense and run back and does not remain so long in contact with the highly heated material.

*e.* Heating in a horizontal glass tube surrounded by a brass block. In this case the tube was of soft glass, 300 mm. long and 22 mm. in diameter, and closed at one end. The block was of cast brass and was 50

mm. square by 300 mm. long. A centrally located hole 25 mm. in diameter extended from one end to the other. The open end of the glass tube was closed by a cork carrying a smaller tube as in *d*. The end carrying the cork projected far enough out of the brass block to avoid burning the cork. The advantage in this method of heating is that the heat is applied regularly throughout the whole length of the tube and the intense local heating, caused by the direct application of the flame, is avoided. As all parts of the tube are above the boiling point of the nitrile, there is no condensation and running back of the nitrile. The brass block was heated by two Bunsen burners properly spaced.

In no case was much trouble experienced with foaming except with the mixture containing zinc thiocyanate. The last two methods gave much purer products, but the yields are much more uncertain, owing to the difficulty of working up the small amounts of the products. The losses of nitrile are proportionately greater than with the larger amounts. With these tubes only small amounts of materials can be used.

**Working up Products.**—The methods of separating the nitriles from the crude distillates were those commonly used in organic preparations.

The distillate containing acetonitrile or butyronitrile was diluted with half its volume of water, treated with solid potassium carbonate or ammonia gas to saturation, the upper layer separated and fractioned. In some cases, the total distillate containing acetonitrile was fractioned up to 85° and the distillate put through this treatment.

Propionitrile was separated by calcium chloride and the upper layer fractioned. Isobutyl cyanide was separated by fractionation.

In the cases of stearic, cinnamic, hydrocinnamic, and phenylacetic nitriles, the crude distillates were treated with a little water and a slight excess of ammonia and steam distilled. The nitrile was separated and the water layer extracted with ether. Stearic nitrile was also separated from the crude distillate by fractionation in a vacuum. It was never obtained pure.

The crude terephthalic nitrile was purified by sublimation. This gave beautiful short white needles melting at about 200°.

**Results.**—The results of the various experiments are brought together below in tables. Under "Ratio" is given the ratio of amount of the thiocyanate used to the calculated amount. Under "Prod." is given the weight of the crude product obtained by the distillation of the mixture of salts, and, in the next column, the weight of the nitrile isolated from such crude product. In the last column is given the yield in per cent. of the calculated.

### Discussion of Results.

From Table I, in which are given experiments in which acetates of various metals were heated with lead thiocyanate, it appears that the

acetates of the most of these metals give considerable yields of the nitrile. Nickel acetate gave little and magnesium acetate none that could be isolated. The distillates in Experiments 7 and 9 from mixtures containing magnesium and barium acetates had fearful, suffocating odors which may have been due to the presence of isocyanates. In an experiment, not included in the table, 75 g. of potassium thiocyanate were heated with 25 g. calcium acetate and only 1.2 g. of crude distillate was obtained. This had a similar bad odor.

TABLE I.  
Acetates of Various Metals Heated with Lead Thiocyanate.

No.	Method.	Acetate.	Pb(CNS) <sub>2</sub> .	Acetate.	Ratio.	Time.	Prod.	Nitrile.	Calc.	Yield.
1	<i>d</i>	Zn	4.0 g.	2.0 g.	1.14	30	4.0 g.	0.2 g.	0.9 g.	22%
2	<i>d</i>	Zn	11.0	5.0	1.25	75	1.4	0.56	2.2	25
3	<i>d</i>	Mn	20.0	9.0	1.20	90	3.0	3.0	4.3	70
4	<i>d</i>	Mn	10.0	4.2	1.28	45	1.1	0.5	2.0	25
5	<i>d</i>	Ni	10.0	5.0	1.37	45	1.5	0.1	2.3	4
6	<i>d</i>	Co	4.0	2.0	1.37	30	0.5	0.2	0.9	22
7	<i>d</i>	Mg	7.0	3.0	1.03	30	0.6	?	...	?
8	<i>d</i>	Sr	6.0	3.4	1.13	45	0.3	0.3	1.4	21
9	<i>d</i>	Ba	6.5	5.0	1.08	45	0.8	0.3	1.6	19
10	<i>c</i>	Cu	90	50	1.00	60	25	6.0	22.6	27
11	<i>c</i>	Pb	120	120	1.00	240	28	5.0	30.3	16
12	<i>c</i>	Pb	85	83	1.00	90	22	6.0	20.9	29
13	<i>c</i>	Pb	95	85	1.12	150	21	6.0	21.5	28

TABLE II.  
Lead, Cuprous, and Zinc Thiocyanates with Zinc Acetate.

No.	Method.	Metal.	<sup>1</sup> M(CNS) <sub>2</sub>	Zn(AcO) <sub>2</sub> .	Ratio.	Time	Prod.	Nitrile.	Calc.	Yield.
1	<i>d</i>	Pb	4.0 g.	2.0 g.	1.14	30	4.0 g.	0.2 g.	0.9 g.	22%
2	<i>d</i>	Pb	11.0	5.0	1.26	75	1.4	0.56	2.2	25
14	<i>d</i>	Cu'	3.0	4.0	0.57	30	0.8	0.4	1.0	40
15	<i>e</i>	Zn	3.0	3.0	0.99	180	0.7	0.4	1.3	31

TABLE III.  
Lead Thiocyanate and Zinc Acetate in Different Proportions and with Different Methods of Heating.

No.	Method.	Pb(CNS) <sub>2</sub> .	Zn(AcO) <sub>2</sub> .	Ratio.	Time.	Prod.	Nitrile.	Calc.	Yield.
16	<i>c</i>	90 g.	50 g.	1.03	210	23.0 g.	9.0 g.	22.4 g.	40%
17	<i>c</i>	72	20	2.05	120	11.0	4.0	8.9	45
18	<i>c</i>	115	60	1.09	195	28.0	15.5	26.8	57
19	<i>c</i>	50	25	1.13	150	7.0	1.4	11.2	12
20	spec.	18	10	1.02	180	3.0	1.0	4.5	22
1	<i>d</i>	4.0	2.0	1.14	30	4.0	0.2	0.9	22
2	<i>d</i>	11.0	5.0	1.26	75	1.4	0.56	2.2	25
21	<i>e</i>	6.0	3.0	1.13	60	1.5	0.8	1.3	61
22	<i>e</i>	6.0	3.0	1.13	60	1.2	0.3	1.3	24
23	<i>e</i>	6.0	3.0	1.13	180	0.6	0.3	1.3	24
24	<i>b</i>	40	20	1.13	180	7.4	4.1	8.9	46
25	<i>b</i>	100	50	1.13	420	19.8	11.3	22.4	50
26	<i>b</i>	140	70	1.13	420	26.5	17.8	31.3	57

<sup>1</sup> M = Pb, Zn, or Cu' as indicated in 3rd column.

TABLE IV.

Zinc Salts of Propionic, Butyric, Isovaleric, Stearic, Phenylacetic, Cinnamic, Hydrocinnamic, and Terephthalic Acids with Lead Thiocyanate.

No.	Meth.	Acid.	Pb(CNS) <sub>2</sub>	Zn $\bar{A}$ <sub>2</sub> <sup>1</sup>	Ratio.	Time.	Prod.	Nitrile.	Calc.	Yield.
27	<i>e</i>	propionic	5.0 g.	3.0 g.	1.09	120	1.5 g.	1.1 g.	1.6 g.	71%
28	<i>c</i>	butyric	35.0	18.0	1.44	150	10.0	3.0	10.4	29
29	<i>e</i>	butyric	4.5	3.0	0.97	90	1.5	1.3	2.1	61
30	<i>b</i>	butyric	30.0	15.0	1.30	120	8.9	5.3	8.6	62
31	<i>e</i>	i.valeric	5.0	3.0	1.38	120	1.3	1.0	1.86	54
32	<i>e</i>	i.valeric	4.0	1.5	2.21	120	0.9	0.8	0.93	86
33	<i>a</i>	stearic	51	100	1.00	90	52	16	84	19
34	<i>a</i>	stearic	60	60	2.00	120	50	5	50	10
35	<i>c</i>	stearic	15	25	1.26	45	22	20	21	95?
36	<i>c</i>	phthalic	45	40	1.16	90	21	15	30	50
37	<i>a</i>	cinnamic	75	50	1.67	240	...	14	44	32
38	<i>a</i>	cinnamic	75	25	3.33	240	...	8	22	36
39	<i>c</i>	cinnamic	63	25	2.97	180	8	6	22	27
40	<i>c</i>	hydrocin.	35	35	1.12	90	21	18	25	72
41	<i>c</i>	hydrocin.	50	25	2.20	60	19	12	18	67
42	<i>d</i>	terephth.	5.0	3.0	1.18	30	1.0	1.0	1.7	59

TABLE V.

Lead Salts of Phenyl Acetic and Cinnamic Acid with Lead Thiocyanate.

No.	Method.	Acid.	Pb(CNS) <sub>2</sub>	Pb $\bar{A}$ <sub>2</sub> <sup>1</sup>	Ratio.	Time.	Prod.	Nitrile.	Calc.	Yield.
43	<i>a</i>	ph. ac.	35 g.	50 g.	1.03	120	15 g.	6.0 g.	24 g.	25%
44	<i>a</i>	cin.	100	75	2.04	150	...	8.0	37	21

In most of the first 9 experiments the amounts of materials used were small and the amounts of acetonitrile worked with were quite small. On this account the losses in handling the nitrile were proportionately great and the results given, representing the amounts isolated, are probably much too low. It appears from these experiments that manganese and zinc acetates are the most suitable for the preparation of the nitrile. The manganese acetate gave a particularly high yield and a clean pure product, but as zinc salts are so much more readily obtained than those of manganese, the zinc salts are to be preferred for practical work.

Experiments 10, 11, 12, and 13 with copper and lead acetates, in glass retorts using larger amounts of materials, are to be compared with Experiments 15, 17, and 18 of Table III in which zinc acetate was used under the same conditions. It thus appears that zinc acetate gives nearly twice the yield that lead acetate does. The stability, fusibility, and mutual solubilities of the fused salts are probably the determining factors in the matter of the yields from various mixtures.

From the results in Table II, it appears that thiocyanates of other heavy metals can be used. In Experiment 14 an excellent yield was obtained from cuprous thiocyanate. In this case the yield is calculated from the thiocyanate present instead of from the acetate as in all the

<sup>1</sup>  $\bar{A}$  stands for one equivalent of the acid indicated by abbreviation in 3rd column.

other experiments. The results obtained with zinc thiocyanate suggest that it might be substituted for the corresponding lead salt to advantage, but its physical properties make against its use. Lead thiocyanate, being insoluble in water, is readily obtained by precipitation, and is easily dehydrated. Zinc thiocyanate is very soluble in water and hence inconvenient to prepare and is difficult to dehydrate. For these reasons the lead salt is better for practical work.

From the results given in Table III, it appears that much better results are obtained by methods *c* and *b* in which larger quantities of materials are used in glass or iron retorts. Contrasting Experiment 16 with Experiment 17 in which double the calculated amount of the lead sulfo-cyanate was used, it appears that little or nothing is gained by the use of this large excess.

From the experiments in Table IV, it appears that the yields are better with the higher molecular weight acids than with acetic, isovaleric giving 86% of the calculated amount of nitrile. This may be only apparent, since the higher nitriles, on account of their being less volatile and less soluble in water, are much easier to isolate than is acetonitrile. The results with stearic acid are not regarded as reliable as no good method is available for the isolation of this nitrile.

Comparing Experiments 37 to 39 with 40 and 41, we see the effect of the ethylene group in cinnamic acid. A much larger yield of hydrocinnamic nitrile is obtained than of the cinnamic. The use of diminished pressure during the distillation in Experiments 37 and 38 did not materially increase the yield. The high yield of hydrocinnamic nitrile, when the mixture of salts is heated in a plain glass retort, is surprising. This shows that the method is available for the preparation of nitriles of high molecular weight, provided there are no interfering groups in the molecule.

In this work, the mixed aromatic-aliphatic acids in which the carboxyl group is not in the ring are considered as aliphatic.

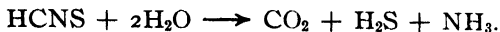
Experiment 42, with terephthalic acid, an aromatic acid, does not properly belong to this study, but was tried to test the applicability of the method for di-nitriles.

The experiments in Table V, with lead salts, are to be compared with those with the corresponding zinc salts in Table IV. The comparison is to the advantage of the zinc salts as it was with the acetates in Table I.

According to Liebig and Rammelsburg<sup>1</sup> and also Voelckel,<sup>2</sup> thiocyanic acid decomposes when heated, in presence of water, into carbon dioxide, carbon disulfide, and ammonia.

<sup>1</sup> *Pogg. Ann.*, **56**, 94 (1842).

<sup>2</sup> *Ibid.*, **58**, 135 (1843); *Ann.*, **43**, 74 (1842).



It was thought that possibly some of these decomposition products might act on the lead salt of an acid to give the nitrile. Accordingly an experiment was performed to determine the effect of the decomposition products of thiocyanic acid on the lead salt of benzoic acid. Dry ammonia was passed through carbon disulfide which was sufficiently warmed to give it the proper vapor tension. The mixture of the vapors of ammonia and carbon disulfide was passed over lead benzoate (39 g.), which was heated in an oil bath to a temperature of  $220^\circ$ . *Results:* a mixture of benzoic acid and benzonitrile condensed on the cooler part of the lead benzoate flask and also in the condenser. A few drops of a pale yellow liquid passed through the condenser. This had an odor of carbon disulfide. All the lead benzoate was converted into a black residue of lead sulfide, with black mirror of same around the upper part of the flask. The amount of benzonitrile formed was insignificant. This shows that readily formed  $\text{CS}_2$  and  $\text{NH}_3$  do not produce the same results as the lead thiocyanate.

In another experiment, a mixture of ammonia and carbon dioxide was passed over a mixture of 35 g. of lead benzoate and 5 g. of sulfur, heated in an oil bath to a temperature of  $240^\circ$ . *Results:* Solid ammonium carbonate was deposited on the walls of the lead benzoate flask and in the condenser and also in the receiver. Sulfur sublimed and deposited on the upper part of the flask. The odor of benzonitrile was apparent but the amount formed was insignificant.

In Experiment 20, to determine whether the nitrile is decomposed by side reactions, etc., into the free acid, the mixture of zinc acetate and lead thiocyanate was heated in an oil bath with reflux condenser. The blackening began between  $150$  and  $170^\circ$  and the reaction began at about  $250^\circ$ . The mixture was kept at this temperature for a considerable time and then the bath was removed and the heating completed with a luminous flame. The nitrile was finally distilled off. The yield was less than usual, showing that prolonged contact of the nitrile with the heated mass lowers the yield.

Stannous and basic ferric acetates were heated with lead thiocyanate but the mixtures did not fuse and gave no nitrile. In the case of the ferric salt, a white solid was deposited in the condenser. This proved to be ammonium carbonate.

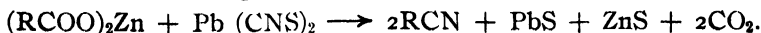
In several experiments, the issuing gases were measured and examined. No hydrogen sulfide was found. A small amount of carbon monoxide was found. The amount of carbon dioxide corresponded closely to that calculated from the reaction given below.

### Conclusions.

1. Aliphatic nitriles, as well as aromatic, are readily prepared, with good yields, by distilling mixtures of well dried heavy metal salts of the acids with slight excess of lead, or other thiocyanate.

2. All things considered, the best mixture is the *zinc* salt of the organic acid with *lead* thiocyanate.

3. The reaction takes place, in the main, according to



4. Excess of the thiocyanate and use of vacuum do not materially increase the yields.

5. *Preparation of Acetonitrile*.—A mixture of one part well dried zinc acetate and two parts, by weight, of lead thiocyanate is heated in a plain glass retort till no more distillate comes over. The crude distillate is mixed with half its volume of water, saturated with solid potassium carbonate or ammonia gas and the nitrile separated and fractioned.

BALTIMORE, MD.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY.]

## STUDIES IN THE PREPARATION OF NITRILES. III. THE CATALYTIC PREPARATION OF NITRILES.

By G. D. VAN EPPS AND E. EMMET REID

Received August 2, 1916.

### Introduction.

Numerous experiments have recently been described, in which substances have been made to react, with elimination of water, by passing them, in vapor form, over certain metallic oxides, notably alumina and thoria. Thus Senderens<sup>1</sup> prepared ethers by passing vapors of the alcohols over alumina at 240–260°. Sabatier and Mailhe<sup>2</sup> found that alcohols yield ethylene hydrocarbons and water with thoria and alumina at 300–350°, and that various phenols<sup>3</sup> when mixed with methyl alcohol give the methyl ethers of the phenols with thoria at 390–420°, or the diphenyl ethers<sup>4</sup> when the alcohol is left out. The same authors<sup>5</sup> found that, when a mixture of the vapors of an acid and an alcohol is passed over titania or thoria at 280°, esterification takes place with great rapidity, the limit of esterification being reached in minutes instead of the hours required at 154° or 200°, without catalyst.

Since the formation of a nitrile from the acid and ammonia



<sup>1</sup> *Compt. rend.*, **148**, 227–8 (1909)

<sup>2</sup> *Ibid.*, **150**, 823–6 (1910).

<sup>3</sup> *Ibid.*, **151**, 359–62 (1910).

<sup>4</sup> *Ibid.*, **151**, 492–4 (1910).

<sup>5</sup> *Ibid.*, **152**, 494–497, 1044–47 (1911), *Chem. Ztg.*, **35**, 193 (1911).



may be regarded as a dehydration reaction, it was thought that it might take place under similar circumstances. The experiments have justified this supposition, since it has been found that excellent yields of acetonitrile may be obtained directly from acetic acid and ammonia, by passing their vapors over alumina or thoria at 500°.

The study of this reaction may throw some light on the mechanism of the other reactions since, in this case, we are well acquainted with ammonium acetate which may be formed as an intermediate product in the reaction.

Acetic acid has been the only acid studied, but it is probable that other acids will yield nitriles under similar circumstances.

As usually made, from acetamide and phosphorus pentoxide, both of which are rather expensive, acetonitrile is an expensive substance and one difficult to prepare in large quantities. By the present method in which it is made in a direct continuous process from acetic acid, and ammonia, both cheap materials, it becomes one of the most accessible compounds.

### Experimental.

**Materials.**—A high grade glacial acetic acid containing very near 100% acid was used. Weighed amounts of this were diluted with weighed amounts of water for the acids of 95%, 90%, etc., strength. The other chemicals used were good commercial products. The ammonia was drawn directly from a cylinder of the liquefied gas.

**The Catalyst.**—Pumice stone, broken to pieces 3 to 5 mm. in diameter, was soaked in a concentrated solution of aluminium sulfate, treated with ammonium hydroxide, and well washed. The pumice stone with the adhering aluminium hydroxide was at first dried in an air bath, but later was dried in the copper tube in a current of ammonia.

For the thoria catalyst, the pumice stone was wet with a concentrated solution of thorium nitrate and heated to about 500° in a current of ammonia.

**Apparatus.**—The catalyst was placed in a very thick walled copper tube 762 mm. long and 32 mm. bore, heated by long burners. This will be more fully described elsewhere. The acid was run in through a brass tube containing a trap to prevent the exit of vapors. This ended about 80 mm. inside the copper tube so that the acid was vaporized on entering. Around this tube was a larger but shorter tube, through which the ammonia was introduced. Thus the acid vapor was introduced directly into an atmosphere of ammonia at the reaction temperature.

The exit end of the copper tube was connected through a Liebig condenser with a receiver from which a tube led to a flask of dilute sulfuric acid to absorb any excess of ammonia gas.

The temperature of the copper tube was measured by an arrangement

by which the expansion of the tube itself was made to move a hand on a dial.

**Procedure.**—The acid or other liquid was dropped into the funnel of the trap tube from a small dropping funnel at a rate of one drop per second. The ammonia was passed in at such a rate that white vapors filled one-half the condenser tube. This shows presence of sufficient excess of ammonia.

Usually the product in the receiver forms two layers, the upper one being nearly pure nitrile, and the lower containing some nitrile and much ammonium acetate. Acetonitrile is salted out of water by ammonium acetate. On completion of each experiment, the upper layer of nitrile was separated and distilled up to 85°. The lower layer was fractionated up to 90°, the fraction being redistilled up to 82–84°. The total nitrile obtained is the sum of these two portions. In cases where no layer was observed the whole product was fractionated up to 90°, the lower fraction being redistilled up to 85°.

**Results.**—The first experiment with alumina at above 500° showed the production of nitrile. Then a large number of experiments were made in order to find the best conditions as to catalyst, temperature, relative amounts of ammonia, etc. The results of these are given below in tabular form.

It was thought possible that ethyl acetate might react with ammonia



and accordingly this was tried with alumina at 510°, but no nitrile was obtained. It is known that acetone passed over pumice at 500° gives ketene<sup>1</sup> which might possibly react with ammonia to form the nitrile.



Accordingly, acetone vapor and ammonia were tried at 500° with alumina, but no nitrile was obtained.

It was thought that acetic anhydride might give better yields with ammonia than acetic acid, since less water would have to be split off. Accordingly, two experiments were tried, using the anhydride at 500–530° and at 520–560°. These gave 31.3 and 24.4% of the calculated amount of nitrile. As these were lower yields than were usually obtained with the 100% acid the use of the anhydride appears to be of no advantage and no further experiments were tried with it. The anhydride would, doubtless, have given better yields with the better catalyst that was used in later work with acetic acid.

In order to ascertain whether a catalyst is required, two experiments were tried in which acetic acid and ammonia were passed through the

<sup>1</sup> Schmidlin and Bergman, *Ber.*, 43, 2821 (1910).

hot tube filled with broken pumice stone at 400° and at 500° but no nitrile could be isolated in either case. The product seemed to be mainly acetamide.

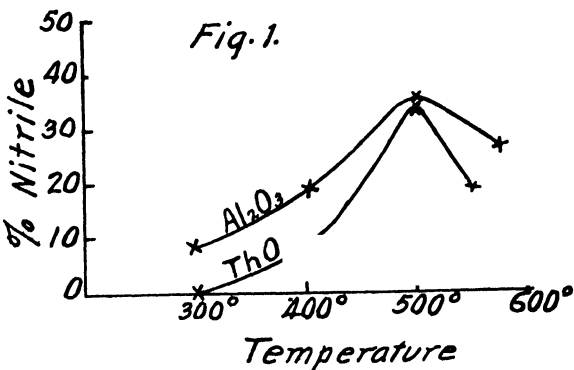
The next experiments were to determine the relative activity of the two catalysts, alumina and thoria at various temperatures with 100% acetic acid. The four experiments with alumina were run with same catalyst without removing it from the copper tube and the four with thoria likewise. The results are given in Table I and graphically in Fig. 1.

TABLE I.

Temp.	Acid used.	Time in minutes.	With thoria.		With alumina.	
			Grams.	Per cent.	Grams.	Per cent.
305°	20.0 g.	..	None	....	....	....
300°	107.5	80	....	....	6.0	8.2
405°	57.9	65	3.5	8.8	....	....
400°	118.0	65	....	....	15.0	18.6
500°	66.0	75	15.4	34.1	....	....
500°	89.0	60	....	....	21.5	35.3
550°	83.5	85	10.5	18.4	....	....
575°	120.0	55	....	....	21.8	26.6

For the lower temperatures the alumina gives decidedly better results. About 500° appears to be the best temperature with both catalysts. The results are plotted in curves with the percentage yield against temperature.

Too much reliance must not be put in these figures, since the results given below show that there is great variation in the yields without apparent cause, and that different preparations of the same catalyst give widely different results. As the alumina appears to be slightly more effective



than the expensive thoria, the alumina catalyst was used exclusively in the remainder of the work. In the experiments at 300° and 400° with both catalysts, acetamide seemed to be present in the product, but it was not positively identified.

The remaining experiments are all given in Table II, the two main variables being percentage of acetic acid and the preparation of the catalyst. Experiments were run with differing concentrations of the acid with one lot of catalyst, and then the copper tube would be cleaned out and another lot of catalyst put in and more experiments run. A blank space

across the table indicates this change to a new lot of catalyst, the double space at Expt. 39 indicates change in method of preparation of catalyst. The temperature was near 500° in all. The experiments are numbered in the order in which they were run.

The catalyst becomes covered with a black deposit and loses its activity. The method of estimating the nitrile gives, only approximate results. It represents not the amount formed, but the amount that may be isolated according to methods in use in ordinary organic preparations. The accuracy of the work naturally increases toward the end.

TABLE II.

No. of experiment.	Strength of acid.	Temperature.		Time in minutes.	Acetonitrile.				Yield in per cent.
		Start.	End.		Upper layer.	Lower layer.	Total.	Calculated.	
1	100%	500-500°		135	....	...	14.8	41.0	36.1
2	100%	520-550°		99	10.7	2.2	12.9	41.0	31.5
3	100%	510-505°		63	16.6	4.3	20.9	41.0	50.2
4	100%	500-500°		42	....	...	18.4	41.0	43.9
5	100%	510-505°		13	....	...	10.1	41.0	24.7
6	90%	505-505°		60	16.9	8.8	25.7	36.9	69.6
7	80%	500-510°		30	11.4	3.9	15.3	32.8	46.6
8	95%	500-505°		45	18.9	3.2	22.1	38.9	56.8
9	95%	500-500°		35	19.7	1.6	21.3	38.9	54.7
10	95%	500-500°		45	22.1	0.9	23.0	38.9	59.1
11	90%	500-520°		35	9.6	3.4	13.0	36.9	35.2
12	90%	505-505°		60	15.6	2.5	18.1	36.9	49.0
13	90%	510-510°		55	12.2	3.1	15.3	36.9	41.4
14	90%	500-505°		35	9.8	2.9	12.7	36.9	34.4
15	90%	510-505°		45	12.0	2.7	14.7	36.9	39.8
16	85%	500-500°		50	9.3	4.3	13.6	34.9	38.9
17	85%	525-510°		45	11.0	4.2	15.2	34.9	43.5
18	85%	505-525°		40	12.4	3.1	15.5	34.9	44.4
19	85%	505-510°		50	15.3	2.5	17.8	34.9	51.0
20	85%	510-510°		40	12.2	3.5	15.7	34.9	44.9
21	80%	500-510°		40	13.4	2.8	16.2	32.8	49.3
22	80%	505-510°		40	13.4	3.4	16.8	32.8	51.2
23	80%	515-510°		45	13.9	1.6	15.5	32.8	47.2
24	75%	510-520°		45	13.2	4.1	17.3	30.8	56.2
25	75%	500-525°		55	9.1	8.2	17.3	30.8	56.2
26	75%	505-520°		65	10.5	6.6	17.1	30.8	55.5
27	70%	500-500°		55	8.0	4.2	12.2	28.7	42.5
28	70%	500-500°		60	4.3	7.7	12.0	28.7	41.8
29	70%	500-500°		50	7.2	5.8	13.0	28.7	45.2
30	95%	500-525°		55	13.0	3.6	16.6	38.9	42.6
31	95%	510-520°		55	18.8	3.7	22.5	38.9	57.7
32	90%	520-525°		65	19.9	5.3	25.2	36.9	68.3
33	90%	500-525°		65	13.8	8.5	22.3	36.9	60.4
34	85%	510-520°		60	10.5	8.5	19.0	34.9	54.4
35	80%	500-525°		65	....	...	16.4	32.8	50.0

TABLE II—(Continued).

No. of experiment.	Strength of acid.	Temperature.		Time in minutes.	Upper layer.	Acetonitrile.			Yield in per cent.
		Start.	End.			Lower layer.	Total.	Calculated.	
36	85%	500	525°	55	10.8	6.6	17.4	34.9	49.8
37	85%	500	520°	70	7.5	10.3	17.8	34.9	51.0
38	75%	500	520°	50	6.6	6.6	13.2	30.8	42.8
39	75%	510	540°	60	....	...	13.8	30.8	44.8
40	75%	520	535°	50	14.9	7.0	21.9	30.8	71.1
41	75%	525	530°	55	13.6	6.9	20.5	30.8	66.5
42	95%	510	525°	65	22.0	6.8	28.8	38.9	74.0
43	95%	505	520°	55	23.9	3.3	27.2	38.9	70.0
44	90%	500	515°	50	16.6	5.6	22.2	36.9	60.1
45	90%	500	515°	60	18.8	4.0	22.8	36.9	61.7
46	85%	515	525°	80	16.1	5.4	21.5	34.9	61.6
47	85%	505	520°	55	16.9	2.0	18.9	34.9	54.1
48	75%	510	530°	60	11.1	5.6	16.7	30.8	54.2
49	100%	510	530°	50	19.9	2.9	22.8	41.0	55.6
50	100%	505	530°	55	25.9	8.8	34.7	41.0	84.6
51	100%	505	530°	75	31.7	3.5	35.2	41.0	85.8
52	95%	510	520°	55	17.9	3.9	21.8	38.9	56.0
53	95%	520	520°	55	25.3	2.4	27.7	38.9	71.2
54	90%	510	520°	60	20.5	3.7	24.2	36.9	65.5
55	90%	510	520°	50	16.3	2.0	18.3	36.9	49.5
56	85%	520	520°	60	16.1	4.5	20.6	34.9	59.0
57	85%	505	520°	55	10.6	4.8	15.4	34.9	41.7

### Discussion of Results.

In Expt. 3 a small excess of ammonia was used and in Expt. 4 a much more rapid current of ammonia. The smaller amount gave 50.2% against 43.9% for the larger. This seems strange, at first sight, but the rapid current of ammonia hurries the acid vapor through the hot tube and does not give it time to react. In Expt. 5 the flow of the acid was four times as rapid as in Expt. 3 and only about half as large a yield of nitrile was obtained, but twice as much nitrile per minute was formed.

A calculation as to the rapidity of the reaction is of interest. Since 60 g. of acetic acid is 1 mol its vapor should occupy at 500°,  $\frac{22.4 \times 773}{273} =$

63 l. = 63,000 cm. As the bore of the tube is 32 mm., its area is 8.0 sq. cm. Dividing 63,000 by 8, we have 7,875 as length of a tube of this size required to contain the acetic acid vapor. In Expt. 50, this amount of acid vapor passed through the tube in 55 minutes, from which the linear velocity of the vapor must be  $7875 \div 55 = 143$  cm. per minute. As the length of the tube is 76.2 cm. the vapor must pass through the tube in one-half minute. This calculation has been made assuming that there is nothing in the tube but acetic acid vapor, while in the actual experiment there was more than an equal volume of ammonia. This more than

doubles the linear velocity and reduces the time that any one portion of the vapor is in the tube to one-fourth of a minute or less. Hence, a mixture of acetic acid vapor and ammonia, at  $500^{\circ}$ , in contact with alumina is 85% transformed to nitrile in less than 15 seconds. If this is the average velocity for the whole mass of vapor, the velocity of the reaction in the layers of the vapor in actual contact with the alumina must be enormous.

It appears from many experiments that the addition of moderate amounts of water to the acetic acid does not prevent the formation of the nitrile. In fact, in the earlier part of the work, it seemed that the yields were increased by the addition of water, but the later and more reliable experiments show a diminution of yield with increase of water present. Since water has a much smaller molecular weight than acetic acid, the molecular percentage of water in the mixture is much larger. The effect of the water is seen from Table III in which some of the experiments from Table II are presented in a different way. In the last column the yields obtained, with the diluted acids, are calculated as per cents. of the yield from 100% acetic acid.

TABLE III.  
Showing Effect of Water on Yield.

Experiment.	Per cent. acid.	Actual yield.	Mol. % of acid.	Yield $\div$ 85.
50	100	84.6	100	100%
51	100	85.8	100	100%
53	95	71.2	85	83%
54	90	65.5	73	77%
56	85	59.0	63	70%

The results are as we should expect from the mass law, since the rate of formation of nitrile appears to be roughly proportioned to the concentration of the acid in every case. The water found in the reaction diminishes the effect of the water initially present so that it is not surprising that the weaker acids give better yields than would be expected from the initial composition of the mixture. Good yields, 42 to 45%, were obtained with even 70% acetic acid. The average of 8 experiments with 75% acid is 56% of nitrile, which is better than any results obtained with 80% acid. It is not safe to draw too definite conclusions, as there is a large variation in the results. This variation comes partly from errors in the method of estimation of the nitrile, but mostly from slight changes of conditions in the various experiments, conditions that it is very difficult to control.

Inspection of consecutive experiments shows that the activity of the catalyst gradually diminishes with use and a jump in the yield is noticed on the introduction of a new lot of catalyst.

In one experiment, not included in the table, ammonium acetate dissolved in an equal weight of acetic acid was used instead of the acid.

Only a little nitrile was obtained. In Expt. 2 the lower layer of the distillate was passed through the apparatus again, but only a small additional amount of nitrile was produced.

It appears from Table II that most of the nitrile is found in the upper layer and, when 100% acid is used, a good yield of the nitrile is obtained even when the lower layer is discarded. As we would expect, in the experiments with weaker acid, particularly the 70% acid, a larger amount, in some cases, half or more of the nitrile, is found in the lower layer.

It is intended to continue this work, particularly with the study of the formation of other nitriles.

### Summary.

1. It is found that acetic acid vapor, mixed with a moderate excess of ammonia and passed over alumina or thoria at 500°, gives a large yield, up to 85%, of acetonitrile.

2. This reaction does not take place in case the catalyst is omitted.

3. The yield depends on the activity of the catalyst and may vary greatly for what appear to be trifling differences in the method of preparation of the catalyst.

4. So far as the present work goes, alumina appears to be the best catalyst and about 500° the best working temperature.

5. This method of preparation of acetonitrile is a continuous process requiring very little attention, and is adapted to use for the preparation of large quantities.

BALTIMORE, MD.

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[CONTRIBUTIONS FROM THE SHEFFIELD CHEMICAL LABORATORY OF YALE UNIVERSITY.]

## RESEARCHES ON AMINES. V. THE STRUCTURE OF VITIATINE. SYNTHESIS OF METHYLETHYLENEDIAMINE.<sup>1</sup>

BY TREAT B. JOHNSON AND GEORGE C. BAILEY.

Received July 26, 1916.

The only compound conforming in constitution to the expression  $C_6H_{14}N_6$ , that is recorded in Richter's *Lexikon der Kohlenstoffverbindungen* is the base *Vitiatine* whose structure has never been established. This interesting substance was isolated by Kutscher<sup>2</sup> from beef extract by precipitation in the form of its gold salt, which gave analytical values agreeing with that calculated for  $C_6H_{14}N_6 \cdot 2HCl \cdot 2AuCl_3$ . Later, during a careful investigation of the nature of the toxic bases in urine, Kutscher<sup>3</sup> identified the same amine and ascribed its origin, in this case to the metab-

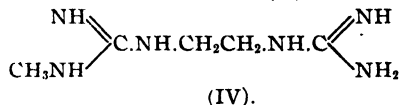
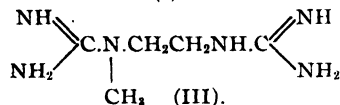
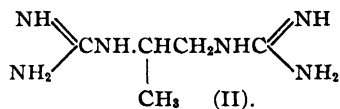
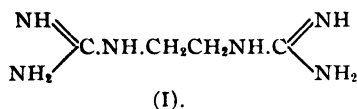
<sup>1</sup> This paper was constructed from a Dissertation presented by Mr. George Corbin Bailey to the Faculty of the Graduate School of Yale University, 1916, in candidacy for the Degree of Doctor of Philosophy.

<sup>2</sup> *Zentr. Physiol.*, 21, 33 (1907).

<sup>3</sup> *Z. physiol. Chem.*, 51, 457 (1907).

olism of flesh food. The following year Engeland duplicated this work of Kutscher's and confirmed his original observations by isolating the same substance in the form of its gold salt from beef extract and urine.<sup>1</sup> Kutscher obtained no chemical evidence upon which to base a structural formula, but assigned to the amine, however, the provisional Formula III, to show its possible relationship to the other bases found with it in urine, *viz.*, guanidine, methylguanidine, dimethylguanidine and creatine.

If *vitiatine* is to be considered as a *mono*-methyl derivative of ethylene-guanidine<sup>2</sup> (I) there are just three structural formulas to which it can theoretically conform, namely: the carbon-substituted derivative represented by Formula II, and the two isomeric nitrogen-substituted compounds corresponding to Formulas III and IV, respectively.



None of these have been prepared. The structure of all three combinations (II, III and IV) would be established by their behavior on hydrolysis. The combinations (II) and (IV) would be productive of diaminopropane<sup>3</sup> (VI) and ethylenediamine (V), respectively, with formation of ammonia and monomethylamine, while a compound having the structure assigned to *vitiatine* (III) would give four proportions of ammonia and monomethylethylenediamine. In other words, the basic nucleus of *vitiatine*, if Kutscher's formula is correct, is the monomethylated base (VII), which has not been described in the literature. The primary object of this investigation was to develop a method of synthesizing this unknown amine.



(V).



(VI).



(VII).

A successful method of synthesizing this compound (VII) was not developed until after we had considered and tried, without success, a number of different methods which seemed feasible of application. No attempts were made by us to prepare the methyl derivative from ethylenediamine by direct alkylation, because Schneider<sup>4</sup> has already shown that this base undergoes exhaustive alkylation by treatment with methyl iodide giving the diquaternary salt  $\text{I}(\text{CH}_3)_3\text{N} \cdot \text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_3\text{I}$ . The

<sup>1</sup> *Z. untersuch. Nahr. und Genussm.*, 16, 658 (1909); *Z. physiol. Chem.*, 57, 49 (1908).

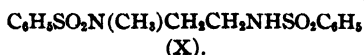
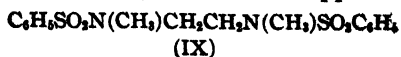
<sup>2</sup> This simple guanidine has never been synthesized.

<sup>3</sup> Hoffmann, *Ber.*, 6, 308 (1873).

<sup>4</sup> *Ber.*, 28, 3073 (1895).



synthesis of the symmetrical dimethyl derivative was accomplished by Schneider by alkylation of the phenylsulfonamide (VIII) with methyl iodide and then hydrolyzing the resulting dialkyl derivative (IX), with hydrochloric acid. He did not succeed in obtaining by alkylation the monomethyl derivative of the sulfonamide (X). We have applied a

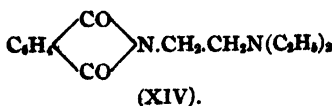
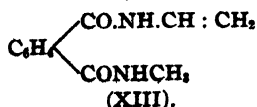
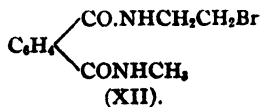
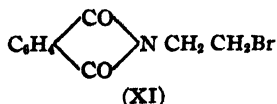


similar reaction with the dibenzylsulfon derivative of ethylenediamine,



and have succeeded in isolating, after alkylation, both the corresponding dimethyl and methyl derivatives. The yield of the latter, however, was so small that the synthesis was of no practical value for the preparation of the free amine. The application of Mendius' reaction was considered by us and the nitrile of sarcosine  $\text{CH}_3\text{NHCH}_2\text{CN}$ <sup>1</sup> and the corresponding phenylsulfon derivative,  $\text{C}_6\text{H}_5\text{SO}_2\text{N}(\text{CH}_3)\cdot\text{CH}_2\text{CN}$ ,<sup>2</sup> were reduced with sodium and alcohol, but in neither case was the operation productive of combinations from which we were able to separate the methyl-ethylenediamine (XII). The action of ammonia on bromoethylmethylamine,  $\text{CH}_3\text{NHCH}_2\text{CH}_2\text{Br}$ , and the corresponding chlorine compound was not investigated. Marckwald and Frobenius,<sup>3</sup> who prepared these amines, have shown that they interact abnormally with alkalis with formation of the cyclicimide,  $\text{CH}_2\cdot\text{CH}_2\cdot\text{N}\cdot\text{CH}_3$ . Bromoethylphthalimide (XI),

also shows irregularities in its behavior towards amines. Ristenpart<sup>4</sup> attempted to prepare the phthalyl derivative of methylethylenediamine by heating this bromide with methylamine, but found, contrary to his expectation, that they interacted in an entirely different manner giving a mixture of the bromoamide (XII), and the corresponding vinyl derivative represented by Formula XIII. Diethylamine, on the other hand, reacted normally with formation of the diamino combination (XIV), but the yield was poor.



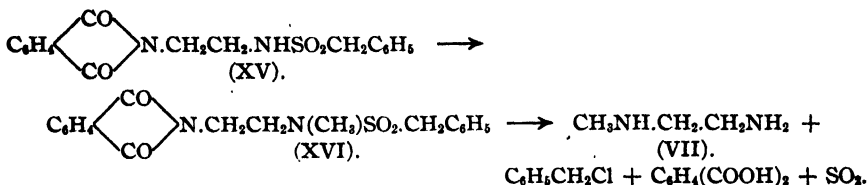
<sup>1</sup> Eschweiler, *Ann.*, 279, 40 (1894).

<sup>2</sup> Johnson and McCollum, *Am. Chem. J.*, 35, 59 (1906).

<sup>3</sup> *Ber.*, 34, 3544 (1901).

<sup>4</sup> *Ibid.*, 29, 2526 (1896).

The synthesis of methylethylenediamine (VII), has now been accomplished by a method which involves the use of bromoethylphthalimide. We find that this halide interacts with the potassium salt of benzylsulfonamide giving the corresponding acid amide (XV). This undergoes alkylation smoothly with methyl iodide, forming the methyl derivative (XVI), which gives on hydrolysis with hydrochloric acid the amine (VII), phthalic acid, sulfur dioxide and benzyl chloride. The transformation is a quan-



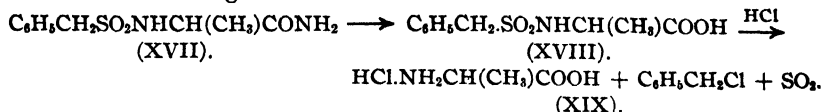
titative one with the exception of the first phase involving the formation of the amide (XV). The first attempts to prepare this were made by allowing the potassium salt of benzylsulfonamide to react with bromoethylphthalimide in alcohol. This method proved a failure as the bromide was decomposed by the alkali with displacement of the halogen by hydroxyl and production of  $\beta$ -hydroxyethylphthalimide.<sup>1</sup> Phenylsulfonamide was tried in place of benzylsulfonamide with the same result. Modifications in procedure were made by changing the strength of alcohol used and varying the time of heating; catalytic agents were introduced and the operation of preparing the salt of the sulfonamide was modified, but in no case was the desired combination formed. Attempts were then made to bring about the change by digesting the bromide with the potassium salt of the amide in benzene, toluene and petroleum ether but no reaction took place under such conditions. Formation of the amide was finally accomplished by fusing the dry potassium salt with bromoethylphthalimide. The best yield, however, that could be obtained by this procedure was 40% of the theoretical. The potassium salt of phenylsulfonamide interacts with bromoethylphthalimide under similar conditions, giving the corresponding phenylsulfonamide (see experimental part).

In the course of our work we had occasion to investigate the behavior on hydrolysis of several alkyl derivatives of benzylsulfonamide. In every case examined, such combinations always broke down when heated with hydrochloric acid with complete destruction of the sulfonic acid. The hydrolysis generally takes place quantitatively below 140°, and by evaporation of the resulting solution the hydrochloride of the amine is obtained free from sulfur compounds. Johnson and Ambler<sup>2</sup> utilized benzylsulfonamide in developing a synthesis of sarcosine. We have ap-

<sup>1</sup> Gabriel, *Ber.*, 21, 572 (1888).

<sup>2</sup> *THIS JOURNAL*, 36, 372 (1914).

plied their method of synthesis and prepared the amino acid—alanine. The potassium salt of benzylsulfonamide interacted smoothly with  $\alpha$ -bromopropionamide in alcohol solution forming the corresponding sulfonamide (XVII). When this was digested with barium hydroxide in aqueous solution it was saponified smoothly with formation of the corresponding acid (XVIII). The latter was decomposed quantitatively when heated with hydrochloric acid at  $130^\circ$ , giving the hydrochloride of alanine (XIX). Benzyl chloride and sulfur dioxide were the secondary products of this change.



Our researches on amines will be continued.

### Experimental Part.

The benzylsulfonchloride which was used in this investigation was prepared according to Pechmann's<sup>1</sup> directions by interaction of phosphorus pentachloride with the sodium salt of benzylsulfonic acid. This was converted into its corresponding amide,  $\text{C}_6\text{H}_5\text{CH}_2\text{SO}_2\text{NH}_2$ , but the action of ammonia.

**Potassium Salt of Benzylsulfonamide,  $\text{C}_6\text{H}_5\text{CH}_2\text{SO}_2\text{NHK}$ .**—This salt was prepared by dissolving a molecular proportion of potassium hydroxide in absolute alcohol and adding to the solution the required amount of the sulfonamide. After heating to boiling for one-half an hour the solution was cooled when the potassium salt separated in the form of micaceous flakes. The salt was separated by filtration and washed carefully with ether. For the success of the next operation this washing was essential in order to remove the mother liquor which contained traces of free alkali and unaltered amide. If dilute alcohol was used the salt separated in a more compact crystalline form and contained little free alkali. The salt did not melt below  $300^\circ$ . It was dried at  $100^\circ$ .

**The Action of Bromoethylphthalimide on the Potassium Salt of Benzylsulfonamide: Phthalimidobenzylsulfonethylenediamine (XV).**—In our preliminary work the potassium salt of benzylsulfonamide was prepared by dissolving 2.2 g. of potassium hydroxide in 40 cc. of alcohol and then dissolving 6.7 g. of the amide in the solution. After boiling for one-half an hour, 10 g. of bromoethylphthalimide were introduced and the solution finally digested until it gave no alkaline reaction. This operation requires from 2 to 3 hours. The precipitate which deposited was filtered off and the mother liquor evaporated to dryness. From the precipitate a theoretical yield of potassium bromide was obtained. The filtrate on evaporation left a yellow, gummy mass, which could not be

<sup>1</sup> Ber., 6, 534 (1873).

crystallized from alcohol, water or ether. The substance became very viscous on warming and solidified to a gum in a freezing mixture. When the material was hydrolyzed in a bomb tube with hydrochloric acid, phthalic acid, benzyl chloride and benzyisulfonamide were formed and identified but no amine was obtained.

A number of experiments were afterwards made using modifications of the above, in which the time of heating, the quantity of alcohol and the strength of the alcohol were varied but without the desired results. It was found that the bromine atom of the phthalimide combination was replaced by a hydroxyl group in the alkaline solution and  $\beta$ -oxyethylphthalimide<sup>1</sup> was formed. The latter compound was isolated and identified by its melting point ( $126-127^\circ$ ). Similar results were obtained by the action of bromoethylphthalimide on an alcoholic solution of the potassium salt of phenylsulfonamide. In every experiment the sulfonamide was recovered unaltered. From these results it was concluded that bromoethylphthalimide cannot be used in alkaline alcoholic solution for such reactions. The above difficulties were finally partially overcome by working under the following conditions:

Molecular proportions of the potassium salt and bromoethylphthalimide were ground together in a mortar and the mixture heated in a flask at  $100-110^\circ$  for 4-5 hours. At the end of this time the melt was a black, viscous liquid, which solidified on cooling. There was no reaction at  $80^\circ$  and no increase in yield was obtained by heating above  $110^\circ$  or longer than 5 hours. This residue was digested with water to remove potassium bromide. After filtering, the residue was subjected to the same treatment several times to remove the last trace of bromide and finally purified by digestion with 50% acetic acid in the presence of animal charcoal. On cooling, the ethylenediamine derivative separated and was further purified by recrystallization from glacial acetic acid. On concentrating the acetic acid filtrates more of the same product was obtained. Glacial or 50% acetic acid were the only solvents in which the compound could be digested with animal charcoal with removal of the coloring material.

From the water filtrate 80% of the theoretical quantity of potassium bromide was isolated, along with unaltered benzyisulfonamide and a low melting substance, which was identified as a mixture of bromoethylphthalimide and the sulfonamide.

The yield of phthalimidobenzyisulfonethylenediamine was 40% of theory. If alkali was present in the potassium salt used in its preparation this yield was decreased and more resinous material was obtained. The compound crystallized from acetic acid in slender prisms which melted at  $175-176.5^\circ$  to a clear oil. It is soluble in benzene, chloroform, methyl

<sup>1</sup> Gabriel, *Ber.*, 21, 572 (1888).

alcohol, ethyl alcohol and acetic acid; insoluble in water and slightly soluble in ether. It was dried for analysis at 100°.

Calc. for  $C_{17}H_{18}O_4N_2S$ : N, 8.14%. Found: N, 7.90, 8.2.

Before using this compound for methylation in the next experiment it was found advisable to crystallize it from alcohol, as there was a tendency for the amide to occlude acetic acid when crystallized from that solvent. Unless this was carefully removed unsatisfactory results were always obtained during alkylation, because the acid present interacted with the sodium alcoholate incorporated and a mixture of unaltered material and the methyl derivative obtained.

**Alkylation of Phthalimidobenzylsulfonamide with Methyl Iodide. Phthalimidobenzylsulfonmethylethylenediamine (XVI).**—Two grams of phthalimidobenzylsulfonethylenediamine were added to 25 cc. of methyl alcohol, in which had been dissolved 0.3 g. of metallic sodium, a slight excess over two molecular proportions. After boiling on the water bath for 45 minutes the solution was cooled and 4 g. of methyl oxide (4 mols) added. The mixture was allowed to stand for a half hour and found to be alkaline; it was then heated to the boiling temperature and digested for an hour or until neutral. Upon cooling the methylated product separated in the form of colorless, prismatic crystals. The yield was 0.7 g. The mother liquor was evaporated to dryness and the residue digested with water until the excess of iodide and alcohol was expelled. An insoluble precipitate was obtained which proved to be the methyl derivative. The total yield of this product was almost theoretical. Sodium iodide was found in the water filtrates in theoretical quantity.

If the original amide was treated with one molecular proportion of sodium instead of two, the methylation was only partially complete and a mixture resulted, from which it was difficult to separate the methylated from the unmethylated amide. Methyl alcohol, as a solvent, gave better results than ethyl alcohol, as in the latter methylation seemed to be incomplete and mixtures resulted from which pure substances could not be isolated. From the analysis of a product obtained under such conditions, it appeared that ethyl groups had replaced the phthalyl group. It was our experience that better yields of the methylated product were obtained when 2 g. portions were alkylated than when larger quantities were taken.

This ethylenediamine derivative crystallized in slender prisms. It is soluble in acetic acid and difficultly soluble in methyl alcohol. It melts at 177–178° to a clear oil. A mixture of this compound and the unmethylated derivative melted at 150–165°.

Calc. for  $C_{18}H_{20}O_4N_2S$ : N, 7.82, S, 8.9. Found: N, 7.94, 7.84, 7.97; S, 8.99.

**Mono-Methylethylenediamine Hydrochloride,  $CH_3NH.CH_2CH_2NH_2 \cdot 2HCl.H_2O$ .**—In order to obtain this salt phthalimidobenzylsulfonmethyl-

ethylenediamine was hydrolyzed by heating with an excess of concentrated hydrochloric acid at  $120^{\circ}$  for 4 hours. At the end of this time benzylchloride had formed a dark layer on the surface of the acid solution and phthalic acid had deposited in a crystalline condition. The contents of the bomb tube were diluted with water, filtered through a wet fluted filter and evaporated to dryness. The colorless residue left behind was triturated with a small amount of cold water and the insoluble phthalic acid filtered off. The aqueous solution of the amine hydrochloride was then evaporated to dryness and the hydrochloride dissolved in boiling 98% alcohol. On cooling, it separated in the form of colorless, micaeous flakes. After recrystallization from 98% alcohol it was then dried for analysis in a vacuum desiccator over concentrated sulfuric acid and potassium hydroxide. When dry hydrochloric acid gas was passed into the alcohol solution the hydrochloride separated very quickly. The amine distils with steam slowly. The hydrochloride melted at  $130-132^{\circ}$  with effervescence and the yield was practically theoretical.

Calc. for  $C_6H_{10}N_2 \cdot 2HCl \cdot H_2O$ : N, 16.98%. Found: N, 17.00, 17.20.

This base is not precipitated from an aqueous solution of its hydrochloride by mercuric chloride. Platinum chloride solution precipitates it from concentrated solutions in the form of square tabular prisms or plates, which melt at  $240-242^{\circ}$  with decomposition. The picrate of the base crystallizes from water in the form of prisms. They turn brown when heated and decompose at  $220-222^{\circ}$  with effervescence.

**Dibenzylsulfonethylenediamine**,  $C_6H_5CH_2SO_2NHCH_2CH_2NHSO_2CH_2C_6H_5$ .—This amide was prepared by heating the potassium salt of benzylsulfonamide with ethylenebromide at  $130^{\circ}$  for 5 hours. At  $110^{\circ}$  a vigorous reaction took place and it was necessary to cool the flask in order to retard the reaction. After the change was complete the reaction product was triturated with ether and the insoluble material washed with water to dissolve potassium bromide. The amide was then purified by crystallization from glacial acetic acid. It melted at  $202-204^{\circ}$ . The yield was 30% of theory. From the ether extract the unaltered dibromide and benzylsulfonamide were recovered. This amide crystallizes in the form of plates.

Calc. for  $C_{16}H_{20}O_4N_2S_2$ : N, 7.60%. Found: N, 7.63, 7.50.

Attempts to improve this yield were unsuccessful. In one experiment 3.6 g. of potassium hydroxide were dissolved in 50 cc. of absolute alcohol 10 g. of benzylsulfonamide were added and the mixture boiled until all the amide dissolved. One-half a molecular proportion of ethylenedibromide (5.4 g.) and 9.5 g. of potassium iodide were added and the solution digested until neutral. On cooling, the amide deposited mixed with potassium iodide and bromide. After washing with water the amide was purified by crystallization from alcohol. It melted at  $202-204^{\circ}$ . The yield

was very small. When ethylenebromide was used in excess the yield was not improved and unaltered amide was always recovered.

This same dibenzylsulfonamide can also be prepared by application of the Schotten and Baumann reaction with ethylenediamine and benzylsulfonchloride. From 5 g. of the amine and 15 g. of the sulfonchloride we obtained 4.5 g. of the purified amide melting at  $204^{\circ}$ . Two and five-tenths grams of acid chloride were recovered and the remainder was decomposed by the alkali.

**The Alkylation of Dibenzylsulfonethylenediamine with Methyl Iodide. The Formation of Dibenzylsulfonmethylethylenediamine,  $C_6H_5CH_2SO_2 \cdot N(CH_3)CH_2CH_2NH \cdot SO_2CH_2C_6H_5$ , and Dibenzylsulfondimethylethylenediamine,  $C_6H_5CH_2 \cdot SO_2 \cdot N(CH_3)CH_2CH_2N(CH_3) \cdot SO_2 \cdot CH_2C_6H_5$ .**—Ten grams of dibenzylsulfonethylenediamine and 2 molecular proportions of potassium hydroxide were dissolved in 150 cc. of 95% alcohol and the solution boiled for one hour. Six grams of methyl iodide were then added and the heating continued until the solution failed to respond to an alkaline reaction. After cooling, the insoluble material was separated and the filtrate saved (see below). This material was washed with cold water to remove potassium iodide and then triturated with a cold 10% solution of sodium hydroxide to remove any monomethylated amide and the insoluble material crystallized from glacial acetic acid. Four grams of material were obtained melting at  $217-219^{\circ}$ .

Calc. for  $C_{18}H_{22}O_4N_2S_2$ : N, 7.07%. Found: N, 7.08, 6.96.

From the alcohol filtrate and the sodium hydroxide washings (after acidifying) 1.5 g. of material were obtained. This product was partly soluble in cold alkali and alcohol. After treatment with alkali and reprecipitating with acid the amide was finally obtained pure and melted at  $137^{\circ}$ . The yield, however, was so small that there was not enough material for hydrolysis.

Calc. for  $C_{17}H_{22}O_4N_2S_2$ : N, 7.33%. Found: N, 7.33, 7.35.

**Dimethylethylenediamine Hydrochloride,  $CH_3NHCH_2CH_2NHCH_3 \cdot 2HCl$ .**—This salt was obtained by hydrolysis of dibenzylsulfondimethylethylenediamine with concentrated hydrochloric acid at  $120-130^{\circ}$ . The contents of the bomb tube were diluted with water, the solution filtered and finally evaporated to dryness. The amine hydrochloride was obtained in a crystalline condition and agreed in melting point and solubility with the dimethylethylenediamine hydrochloride described by Schneider.

**Phthalimidophenylsulfonethylenediamine,**  $C_6H_4 \begin{array}{c} \diagup CO \\ \diagdown CO \end{array} N \cdot CH_2CH_2 \cdot$

$NHSO_2C_6H_5$ .—This was obtained by heating 2.2 g. of bromoethylphthal-

imide with 1.7 g. of the potassium salt of phenylsulfonamide for 4 hours at 100°. After washing with water to remove potassium bromide the amide was decolorized by digesting in 50% acetic acid with animal charcoal and then recrystallized from this same solvent. It crystallized in short, flat prisms which melted at 175°.

Calc. for  $C_{16}H_{14}O_4N_2S$ : N, 8.50%. Found: N, 8.8.

**Di-(*p*-nitrobenzyl)-benzylsulfonamide**,  $C_6H_5CH_2SO_2N(CH_2.C_6H_4NO_2)_2$ .—This amide and its corresponding *mono*-nitrobenzyl derivative were formed by alkylation of benzylsulfonamide with *p*-nitrobenzylchloride. They were separated by trituration with dilute sodium hydroxide solution (10%). The disubstituted derivative was insoluble and was purified by crystallization from glacial acetic acid. It separated in needles and melted at 193–194°.

Calc. for  $C_{21}H_{19}O_6N_3S$ : N, 9.52%. Found: N, 9.40, 9.39.

Acids precipitated from the alkaline washings the *mono*-nitrobenzylbenzylsulfonamide,  $C_6H_5CH_2SO_2NHCH_2C_6H_4NO_2$ . This was purified by crystallization from glacial acetic acid and melted at 182–183°. The yield was small.

Calc. for  $C_{14}H_{14}O_4N_2S$ : N, 9.15%. Found: N, 9.20.

**Di-(*o*-nitrobenzyl)-benzylsulfonamide**,  $C_6H_5CH_2SO_2N(CH_2.C_6H_4NO_2)_2$ .—This crystallized from glacial acetic acid in prisms, which melted at 169–170°.

Calc. for  $C_{21}H_{19}O_6N_3S$ : N, 9.52%. Found: N, 9.35, 9.32.

***o*-Nitrobenzylbenzylsulfonamide**,  $C_6H_5CH_2SO_2NHCH_2C_6H_4NO_2$ .—This crystallizes from alcohol and melts at 124–126°. It is soluble in 10% sodium hydroxide solution.

Calc. for  $C_{14}H_{14}O_4N_2S$ : N, 9.15%. Found: N, 9.0, 8.9.

**Preparation of Di-(*o*-nitrobenzyl)amine Hydrochloride**,  $(NO_2.C_6H_4CH_2)_2NH.HCl$ .—This was easily obtained by heating its corresponding sulfonamide (see above) with concentrated hydrochloric acid at 130–140°. It melted at 245° after crystallization from water. Gabriel and Jansen<sup>1</sup> have described this salt and assigned to it a melting point of 220°.

Calc. for  $C_{14}H_{13}O_4N_3.HCl$ : N, 12.9%. Found: N, 12.3, 12.4.

**Di-(*p*-nitrobenzyl)amine Hydrochloride**,  $(NO_2.C_6H_4CH_2)_2NH.HCl$ .—This was obtained by hydrolysis of its sulfonamide with strong hydrochloric acid. It crystallized from water and melted at 212°. Strakosch<sup>2</sup> has described this salt and assigned to it a melting point of 212°.

Calc. for  $C_{14}H_{13}O_4N_3.HCl$ : N, 12.9%. Found: N, 12.9.

<sup>1</sup> *Ber.*, 24, 3093 (1891).

<sup>2</sup> *Ibid.*, 6, 1056 (1873).



**Benzylsulfonaminopropionamide, (XVII).**—The  $\alpha$ -bromopropionbromide used in this experiment was prepared according to the directions of Zelinsky<sup>1</sup> and converted into the corresponding  $\alpha$ -bromopropionamide by the method described by Bischoff.<sup>2</sup> Twenty-eight and two-tenths grams of benzylsulfonamide were converted into its potassium salt and the latter digested in alcohol with 25 g. of  $\alpha$ -bromopropionamide for 6 hours. The liquor was still alkaline at the end of this time due to the presence of ammonia formed by hydrolysis. On cooling the propionamide deposited mixed with potassium bromide. This was washed with water and purified by recrystallization from hot water. It crystallized in prisms and melted at 167°. The compound is soluble in alcohol, water and acetic acid, and difficultly soluble in benzene and ether. The yield was 15 g.

Calc. for  $C_{10}H_{14}O_2N_2S$ : N, 11.57%. Found: N, 11.6, 11.56.

**Benzylsulfonalanine, (XVIII).**—The amide described above was hydrolyzed by boiling with a strong aqueous solution of barium hydroxide or until no ammonia was evolved. The barium was then exactly precipitated as barium sulfate and the filtrate evaporated to dryness. The acid remained as a crystalline residue and was purified by crystallization from boiling water. It separated in the form of plates which melted at 164–165°. A mixture of this with the unaltered amide melted at 155°.

Calc. for  $C_{10}H_{14}O_4NS$ : N, 5.75; S, 13.16. Found: N, 6.0, 5.8; S, 13.6.

**Hydrolysis of Benzylsulfonalanine with Hydrochloric Acid. Alanine Hydrochloride, (XIX).**—This change was accomplished by heating the sulfonamide with hydrochloric acid for 2 hours at 130°. After filtering the solution was evaporated to dryness and the alanine hydrochloride purified by crystallization.<sup>3</sup>

Calc. for  $C_3H_7O_2N.HCl$ : N, 11.2%. Found: N, 11.3.

NEW HAVEN, CONN.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY.]  
**ON THE REACTION OF BOTH THE IONS AND THE NONION-  
 IZED FORMS OF ACIDS, BASES AND SALTS: THE REAC-  
 TION OF METHYL IODIDE WITH SODIUM, POTAS-  
 SIUM AND LITHIUM ETHYLATES AT 0°.**<sup>4</sup>  
 [TWENTY-FOURTH COMMUNICATION ON CATALYSIS].

BY BESSIE M. BROWN AND S. F. ACREE.

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A theory concerning chemical reactions was brought out by Brunel<sup>5</sup> and one of us in 1905–6, and Johnson<sup>6</sup> in 1907, when they showed by ex-

<sup>1</sup> *Ber.*, 20, 2026 (1887).

<sup>2</sup> *Ibid.*, 30, 2312 (1897).

<sup>3</sup> Strecker, *Ann.*, 75, 29 (1850).

<sup>4</sup> We are indebted to the Carnegie Institution of Washington for aid in this work.

<sup>5</sup> *Am. Chem. J.*, 43, 505 (1910).

<sup>6</sup> *Ibid.*, 38, 259, 260 (1907).

perimental evidence that, in some catalytic reactions, the acceleration may take place not only through the action of the ions, but also to a large extent through the nonionized portion of the salt.

The work of Shadinger,<sup>1</sup> and later, Nirdlinger and Rogers,<sup>2</sup> and Chandler,<sup>3</sup> showed that in absolute alcohol both the 1-phenyl-3-thiouazole anions and the nonionized sodium 1-phenyl-3-thiouazole react with alkyl halides.

In working with the phenolates, Robertson<sup>4</sup> found that both the phenolate ion and the nonionized sodium phenolate react with the alkyl halides, and Marshall,<sup>5</sup> Harrison,<sup>6</sup> and Myers<sup>7</sup> observed that both the ions and molecules of sodium, potassium and lithium ethylates are concerned in the catalytic effect of these compounds on the reversible addition of alcohol to acetonitrile, benzonitrile, *p*-bromobenzonitrile and others.

Other reactions studied, and which uphold this theory, are those of methyl iodide, ethyl iodide, and ethyl bromide with sodium, lithium, and potassium ethylates at 25°.

Any results which shed light upon the mechanism of organic reactions are of such extreme importance, that it was considered advisable to extend this study to other reactions, and to study some of the same reactions at different temperatures. Since at different temperatures the per cent. of ionization changes, it might be possible to decide whether the nonionized molecule or both ions together react, as we have pointed out in earlier articles,<sup>8</sup> and especially for the reactions of water.<sup>9</sup>

With this idea in view, the authors took up the study of the reactions of sodium, lithium, and potassium ethylates with methyl iodide at 0°, and also the effect of added sodium iodide on the reaction between sodium ethylate and methyl iodide at 25° which will appear in a later publication.

If both the ethylate ion and the nonionized ethylate salt react with the molecular alkyl halide, we have two reactions proceeding simultaneously, one proportional to the ionized part of the ethylate,  $\alpha$ ,<sup>10</sup> and the other proportional to the nonionized part,  $1 - \alpha$ . It follows that

<sup>1</sup> *Am. Chem. J.*, **39**, 275 (1908).

<sup>2</sup> *Ibid.*, **49**, 116 (1913).

<sup>3</sup> Dissertation, Johns Hopkins University, 1912.

<sup>4</sup> Dissertation, Johns Hopkins University, 1910; *Am. Chem. J.*, **43**, 519; **49**, 474; *This Journal*, **37**, 1902.

<sup>5</sup> *Am. Chem. J.*, **49**, 127, 369 (1913); *J. Phys. Chem.*, **19**, 589 (1915).

<sup>6</sup> Dissertation, Johns Hopkins University, 1912.

<sup>7</sup> *Am. Chem. J.*, **49**, 122, 132, 485 (1913).

<sup>8</sup> *Ibid.*, **48**, 374-377 (1912); **49**, 350-351, 378-382, 396, 403 (1913). Chandler, Diss.

<sup>9</sup> *Am. Chem. J.*, **41**, 466-483 (1909); **48**, 369-372 (1912); *J. Phys. Chem.*, **19**, 594 (1915).

<sup>10</sup> These values were obtained by Dr. H. C. Robertson, *J. Phys. Chem.*, **19**, 381 (1915), to whom we are greatly indebted.

$$(1) \frac{dx}{dt} = K_i \alpha (C_{\text{ethylate}} - x)(C_{\text{alkyl halide}} - x) + K_m (1 - \alpha)(C_{\text{ethylate}} - x)(C_{\text{alkyl halide}} - x),$$

in which  $K_i$  is the velocity constant for the ionic reaction, and  $K_m$  is the constant for the molecular reaction in a normal solution, and  $x$  is the change in the concentration in the time  $t$ . If A represents  $C_{\text{ethylate}}$ , and B is substituted for  $C_{\text{alkyl halide}}$  we obtain by integration the equation

$$(2) K_N = VK_V = K_i \alpha + K_m (1 - \alpha) = \frac{1}{At} \frac{x}{(A - x)} \text{ if } C_{\text{ethylate}} \text{ is equal to } C_{\text{alkyl halide}},$$

or

$$(3) K_N = VK_V = K_i \alpha + K_m (1 - \alpha) = \frac{1}{(B - A)t} \ln \frac{A(B - x)}{B(A - x)}$$

if  $C_{\text{ethylate}}$  is not equal to  $C_{\text{alkyl halide}}$ .

Substituting the data obtained for  $t$ ,  $x$ , A, and B, we obtain a set of constants for  $K_V$  and  $K_N$  for each concentration of ethylate used.  $K_N$  represents the molecular velocity constant, or the velocity which that reaction would have if the concentration were normal, but the ionization corresponds to the concentration  $1/V$ , when  $V$  is the number of liters containing one gram molecule. For each ethylate there are given two representative tables, I to VI, inclusive, showing the values of  $K_V$  for the different time periods and the average  $K_V$  and  $K_N$  for the particular value of  $V$ . In Tables VII, VIII and IX, are given the summaries for  $K_N$  for all of our 55 duplicate tables<sup>1</sup> corresponding to I to VI. To determine  $K_i$  and  $K_m$  for the separate ionic and molecular reactions, it is only necessary to substitute the proper values in the following simultaneous equations and solve for  $K_i$  and  $K_m$ :

$$K_N = K_i \alpha + K_m (1 - \alpha)$$

$$K'_N = K_i \alpha' + K_m (1 - \alpha'), \text{ etc.}$$

Values for  $K_i$  and  $K_m$  are thereby obtained for every pair of concentrations, and the average of these is taken as the accepted value, and recorded in Table X. By substituting in the equation  $K_N = K_i \alpha + K_m (1 - \alpha)$ , these values found for  $K_i$  and  $K_m$  and the values for  $\alpha$  and  $(1 - \alpha)$  corresponding to the different concentrations of the various ethylates, we obtain the theoretical values for  $K_N$  given in Tables VII, VIII and IX, under the heading " $K_N$  calculated." These are compared with the corresponding values of " $K_N$  found," and the experimental errors, called "Per cent. error," are thus obtained. The percentage of the reaction due to the ethylate ions is given under  $K_i \alpha / K_N$  and the percentage due to the nonionized ethylate molecules is given under  $K_m (1 - \alpha) / K_N$ . For a complete mathematical and theoretical discussion of these equations,

<sup>1</sup> See B. M. Brown, Dissertation, Johns Hopkins University, 1913.

see Johnson and Acree,<sup>1</sup> and the dissertations of Robertson<sup>2</sup> and of Harrison.

Robertson<sup>2</sup> and Marshall<sup>3</sup> discussed the possibility and probability of other reactions taking place simultaneously with those given above. We must consider, for example, the catalytic effect of the salt formed, or even of the ethylate itself, which we could designate as a "salt effect," and perhaps a side reaction, as well, in which olefines may be formed.

Since we obtain, however, from the equations used two constant values for  $K_i$  and  $K_m$ , we can state that we have either two reactions, or two or more sets of reactions, taking place, one being a function of the concentration of the ions, and the other of the nonionized portion.

If  $K_i$  represents the velocity constant of the reaction between the ethylate ion  $C_2H_5O^-$ , and methyl iodide, we would expect to find experimentally that the value for  $K_i$  is the same whether the methyl iodide is allowed to react with sodium, lithium, or potassium ethylates. Considering the greater difficulty in carrying out these reactions at  $0^\circ$  and the possibility of greater errors, there is quite satisfactory agreement between the values of  $K_i$  for the sodium, potassium, and lithium ethylates, namely, 0.00486, 0.00525, and 0.00524, respectively. Dr. W. A. Taylor<sup>4</sup> also obtained the value  $K_i = 0.00496$  for sodium ethylate. The values for  $K_m$  would not necessarily be the same, and might be entirely different, because of the fact that the nonionized molecules of these three ethylates are different substances. In conformity with the theory we find the values 0.00303, 0.00337 and 0.00197 for  $K_m$  for sodium, potassium, and lithium ethylates, respectively, and Dr. W. A. Taylor's value 0.00294 for  $K_m$  for sodium ethylate agrees well with ours. The lower activity for the molecules of lithium ethylate has been observed in every one of a large number of other reactions.

Since viscosity may play an important part in the reaction velocities at  $0^\circ$ , especially in the more concentrated solutions, it will be extremely interesting, as well as important, to obtain all the necessary data, so that corrections can be made for the viscosity, and all other important physical factors.

To make the constants from the different concentrations of ethylate comparable, the reactions were allowed to run to about the same percentage completion, which was usually 50 to 60%, and an average value for the reaction velocity was obtained by taking the mean of the constants for the different time periods. When the last constants were low they were in some cases omitted and the remaining values averaged and

<sup>1</sup> *Am. Chem. J.*, 37, 410 (1907), 38, 258 (1907), 48, 352 (1912).

<sup>2</sup> Dissertation, *loc. cit.*; THIS JOURNAL, 37, 1903, 1908 (1915)

<sup>3</sup> *J. Phys. Chem.*, 19, 594, 602, 607 (1915)

<sup>4</sup> Dissertation, Johns Hopkins University, 1914, p. 19. *J. Phys. Chem.*, 20, 365 (1916).

It will be seen from the results that it makes very little difference in the calculated values for  $K_N$  when these starred values are used in place of the other values.

In the case of lithium ethylate the reaction was so much slower than in the other cases, that it was difficult to obtain the desired time periods, since it was, of course, impossible to titrate by artificial light. For this reason, in some of the more dilute solutions the reactions were 70 to 80% completed. But since the constants in these solutions did not decrease appreciably, there is practically no change introduced by using these values for the longer time periods.

It can be seen from the tables that there is very little difference between the values of  $K_N$  for the different concentrations of potassium ethylate, and that in some of the more dilute solutions, the values vary to such an extent that they nearly overlap for the different concentrations. The only remedy for this is to diminish the error as much as possible by taking the average of a large number of determinations. It was impossible to use solutions more concentrated than  $N/4$  because the potassium iodide formed precipitated out almost immediately, and the ionization of the remaining potassium ethylate consequently changed. It was, therefore, thought advisable to find values for  $K_N$  for  $3N/16$  and  $3N/32$  potassium ethylate so as to give a few more calculated values for  $K_i$  and  $K_m$  and reduce the error.

It can be seen from the data given that the work at 0° is not quite as satisfactory as that at 25°. Although four significant figures are given in some of the tables, the experimental errors vary from 1 to 2%.

### Experimental.

**Preparation of Materials.**—The method used in preparing the solutions and carrying out the reactions at 25° is described in detail by Robertson.<sup>1</sup>

The methyl iodide used was of special purity. To insure a large yield of a constant boiling material, two kilograms of the alkyl halide were shaken with dilute sodium carbonate solution to remove any traces of hydriodic acid, washed twice with water, and then shaken for a few minutes with anhydrous sodium sulfate, and filtered through glass wool. A considerable quantity of phosphorus pentoxide was added and allowed to remain overnight, after which the methyl iodide was distilled. This treatment with the phosphorus pentoxide was repeated, and the product thus obtained was fractionated. Special care was taken to have the condenser and all apparatus perfectly dry, and with these precautions, a product was obtained, the total quantity of which boiled within a few hundredths of a degree. A table is given below showing the boiling points of the different fractions, the barometric pressure and the boiling points at 760 millimeters after all the necessary corrections are made.

<sup>1</sup> *Loc. cit.*

Observed b. p.	Barometer.	Corrected b. p.	Observed b. p.	Barometer.	Corrected b. p.
42.80-42.83	769.4 mm.	42.31-42.33°	42.91-42.86	770.6 mm.	42.35-42.35°
42.82-42.82	769.3	42.33-42.35	42.86-42.82	769.5	42.35-42.34
42.82-42.81	769.3	42.34-42.33	42.82-42.80	768.9	42.34-42.34
42.81-42.81	769.2	42.33-42.33	42.80-42.78	768.2	42.34-42.36
42.93-42.91	771.2	42.35-42.35	42.78-42.79	767.7	42.36-42.37

The rise in boiling point observed in the last fraction was probably due to superheating. No correction was necessary for the exposed stem, because the distilling flask with a long neck made especially for the purpose was used, which made it possible to surround the total column of mercury with the vapor of the alkyl halide. In correcting for the atmospheric pressure the value used was 0.03° per millimeter. The total amount of methyl iodide recovered in these ten fractions was 1,772 g. out of the 2,000 g. used. This is a very satisfactory yield for such a volatile substance. In order to decrease the loss due to the volatility of the methyl iodide, ice-water was continually run through the condenser by means of a fine lead coil of several turns surrounded by ice, and the receiving bottles cooled by ice-water and fairly tightly stoppered with cotton. Another sample purified in the same way boiled at 42.34-42.36°. A sample purified in the same way but distilled with the stem exposed and without special precautions boiled at 42.30-42.32°. A sample of good methyl iodide stood over summer and was then distilled once from phosphorus pentoxide. When fractionated it gave a large middle portion boiling at 42.34-42.36°. Another sample of methyl iodide made by the method used by Robertson boiled at 42.35-42.39°.

It would seem from the boiling points obtained that the methyl iodide used in the reactions was of especial purity. Nevertheless, it was not only a wise precaution but a point of great interest to determine the composition of such samples by analysis.

Satisfactory results were obtained by using small weighing tubes with ground glass stoppers which were especially made for the purpose and held about 2 cc. The alkyl halide could thus be weighed accurately and without loss. The weighing tube containing the alkyl halide was then placed in a regular Carius tube containing an excess of sodium ethylate, sealed, and heated a sufficient length of time in a water bath. It was necessary, of course, to mix the contents thoroughly before heating. The stopper in the little weighing tube was easily removed by warming the tube slightly and then shaking it gently. When the reaction was complete the contents of the tube were washed into a beaker, and then filtered into a calibrated flask, diluted to the mark and weighed. Each portion taken out for analysis was then weighed, since this procedure was much more accurate than the volume method.

In the following analyses Sample I and Sample II are taken from different samples of methyl iodide.

Sample I.					Sample II. B.				
AgI obt.	Air wt.	AgI calc.	Vac. wt.	% error.	AgI obt.	Air wt.	AgI calc.	Vac. wt.	% error.
2.0346		2.0327		+0.12	1.7232		1.7243		—0.03
2.0336		2.0339		+0.01	1.7264		1.7280		—0.08
1.9956		1.9953		+0.04	1.7271		1.7273		+0.01
Sample II. A.					Sample II. C.				
1.5890		1.5889		+0.02	1.5493		1.5500		—0.03
1.5886		1.5889		0.00	1.5489		1.5495		—0.02
1.5894		1.5898		0.00	1.5488		1.5499		—0.05

It is seen that we can easily make alkyl halides with a high degree of purity and that this method of analysis is very accurate. The percentage error is corrected to vacuum weights.

**The Machine.**—Since methyl iodide is so very volatile it would be impossible to transfer the solution to the reaction flasks by the use of an ordinary pipet, without losing a large amount of the alkyl halide. A special apparatus called the "machine" was devised to transfer these solutions with the least possible loss. This machine was described in detail by Robertson.

A large number of determinations were also carried out to see whether the 0.3% excess of methyl iodide ordinarily added was sufficient to make up for any loss of the alkyl halide during the preparation and transfer of the solution. While keeping the conditions the same as those used for studying the reactions, 10 cc. of the solution were run into a small reaction flask containing a 50% alcoholic solution of silver nitrate. The results obtained are given in the tables below. The calculated values given for the silver iodide include the excess added which is given in the parentheses under "Strength of solution."

At 0°.				At 25°.			
AgI obt.	AgI calc.	Strength of soln.	% error.	AgI obt.	AgI calc.	Strength of soln.	% error.
1.1743 <sup>1</sup>	1.1799	(100.5%)	—0.47	2.3535	2.3550	(100.1%)	—0.06
1.1729 <sup>1</sup>	1.1799	(100.5%)	—0.60	2.3500	2.3550	(100.1%)	—0.21
1.1730 <sup>1</sup>	1.1799	(100.5%)	—0.60	2.3424	2.3550	(100.1%)	—0.11
2.3584	2.3598	(100.5%)	—0.06	2.3570	2.3620	(100.6%)	—0.21
4.7279	4.7288	(100.7%)	—0.02	2.3533	2.3597	(100.5%)	—0.27
2.3576	2.3621	(100.6%)	—0.20	1.1727	1.1775	(100.3%)	—0.40
2.3583	2.3621	(100.6%)	—0.16	1.1712	1.1775	(100.3%)	—0.53
2.3542	2.3598	(100.5%)	—0.22				
4.7057	4.7101	(100.3%)	—0.09			Average,	—0.26
2.3495	2.3598	(100.5%)	—0.43				

Average, —0.27

The average of the above analyses shows that the 0.3% excess of methyl iodide seems to be sufficient, although there is considerable variation in the results. However, in a number of reactions 0.5% excess was added.

<sup>1</sup> Same solution.

## Reaction Velocities at 0°.

For the study of the velocity of the reaction between methyl iodide, sodium, lithium, and potassium ethylates at 0° an ice bath was used which gave very satisfactory results. This consisted of a copper bath ten inches deep and fourteen inches in diameter which was tinned on the inside, and placed in a wooden box containing lamb's wool. The bottom was protected with a thick felt pad about one inch thick, and the top by a tightly fitting metal cover, over which were placed several pads of felt and wool. The metal cover was made in two pieces, one of which was removed when it was necessary to take out the flask, start the reaction, etc. Special attention is called to the stirring device. The motor is supported by an iron framework which is bolted firmly to the wall to prevent vibration. Motion is imparted to the propeller shaft by a friction pulley, by means of which the speed can be easily controlled.

TABLE I.—0.5 *N* SODIUM ETHYLATE AND 0.5 *N* METHYL IODIDE AT 0°.

A = 10.00.		
<i>t</i> .	<i>x</i> .	K <sub>v</sub> .
150	2.058	0.001728
180	2.342	0.001700
210	2.634	0.001703
240	2.896	0.001698
2728	8.200	0.001670
<hr/>		
Average, 0.001700		
K <sub>N</sub> , 0.003400		

TABLE II.—0.03125 *N* SODIUM ETHYLATE AND 0.25 *N* METHYL IODIDE AT 0°.

A = 10.01. B = 80.00.		
<i>t</i> .	<i>x</i> .	K <sub>v</sub> .
673	4.970	0.0001321
751	5.338	0.0001319
821	5.562	0.0001287
899	5.874	0.0001284
966	6.314	0.0001353
1095	6.714	0.0001337
<hr/>		
Average, 0.0001317		
K <sub>N</sub> , 0.004212		

TABLE III.—0.25 *N* POTASSIUM ETHYLATE AND 0.25 *N* METHYL IODIDE AT 0°.

A = 10.00.		
<i>t</i> .	<i>x</i> .	K <sub>v</sub> .
110	0.972	0.000980
190	1.600	0.001002
290	2.268	0.001015
350	2.604	0.001006
390	2.804	0.000997
1430	5.936	0.001021
1590	6.196	0.001024
<hr/>		
Average, 0.001006		
K <sub>N</sub> , 0.004024		

TABLE IV.—0.125 *N* POTASSIUM ETHYLATE AND 0.50 *N* METHYL IODIDE AT 0°.

A = 10.00. B = 40.00.		
<i>t</i> .	<i>x</i> .	K <sub>v</sub> .
190	3.192	0.0005285
240	3.832	0.0005311
290	4.376	0.0005282
330	4.792	0.0005299
360	5.064	0.0005280
390	5.360	0.0005331
460	5.880	0.0005271
<hr/>		
Average, 0.0005294		
K <sub>N</sub> , 0.004275		

TABLE V.—0.5 *N* LITHIUM ETHYLATE AND 0.5 *N* METHYL IODIDE AT 0°.

A = 9.98.		
<i>t</i> .	<i>x</i> .	K <sub>v</sub> .
180	1.782	0.001207
240	2.226	0.001196
300	2.643	0.001200
382	3.156	0.001210
1278	5.946	0.001153
1667	6.580	0.001161
<hr/>		
Average, 0.001188		
K <sub>N</sub> , 0.002381		
K <sub>N</sub> , <sup>1</sup> 0.002411		

TABLE VI.—0.03125 *N* LITHIUM ETHYLATE AND 0.25 *N* METHYL IODIDE AT 0°.

A = 10.00. B = 80.00.		
<i>t</i> .	<i>x</i> .	K <sub>v</sub> .
561	3.840	0.0001108
647	4.328	0.0001129
816	5.000	0.0001100
898	5.296	0.0001090
983	5.664	0.0001107
1053	5.928	0.0001114
2086	8.168	0.0001087
<hr/>		
Average, 0.0001105		
K <sub>N</sub> , 0.003536		

<sup>1</sup> If last two values of K<sub>v</sub> are omitted.



TABLE VII.— $K_N$  FOUND,  $K_N$  CALCULATED,  $\alpha$ ,  $(1 - \alpha)$ , ERROR IN PER CENT., AND PER CENT. OF REACTION DUE TO IONS AND TO MOLECULES FOR SODIUM ETHYLATE AND METHYL IODIDE AT 0°.

V.	$\alpha$ .	$1 - \alpha$ .	$K_N$ found.	Av. $K_N$ .	$K_N$ calc.	% error.	Per cent. of reaction due to ions: $K_i\alpha/K_N$ .	Per cent. of reaction due to molecules: $K_m(1-\alpha)/K_N$ .
1	0.136	0.864	0.003299 0.003264	0.003281	0.003282	-0.03	0.21	0.79
2	0.237	0.763	0.003400 0.003420					
			0.003485	0.003435	0.003466	-0.90	0.34	0.66
4	0.335	0.665	0.003679					
			0.003621	0.003650	0.003645	+0.13	0.46	0.54
8	0.435	0.565	0.003825					
			0.003854	0.003840	0.003828	+0.31	0.57	0.43
16	0.531	0.469	0.003919 0.003985					
			0.004063					
			0.004077	0.004011	0.004004	+0.17	0.66	0.34
32	0.633	0.367	0.004212 0.004130					
			0.004165	0.004169	0.004190	-0.50	0.76	0.24

TABLE VIII.— $K_N$  FOUND,  $K_N$  CALCULATED,  $\alpha$ ,  $(1 - \alpha)$ , ERROR IN PER CENT., AND PER CENT. OF REACTION DUE TO IONS AND TO MOLECULES FOR POTASSIUM ETHYLATE AND METHYL IODIDE AT 0°.

V.	$\alpha$ .	$1 - \alpha$ .	$K_N$ found.	Av. $K_N$ .	$K_N$ calc.	% error.	Per cent. of reaction due to ions: $K_i\alpha/K_N$ .	Per cent. of reaction due to molecules: $K_m(1-\alpha)/K_N$ .
4	0.365	0.635	0.004024 0.003982					
			0.004088	0.004031	0.004055	-0.62	0.47	0.53
16/3	0.401	0.599	0.004123					
			0.004124	0.004124	0.004123	+0.02	0.50	0.50
8	0.459	0.541	0.004224					
			0.004235					
			0.004258	0.004239	0.004233	+0.12	0.56	0.44
32/3	0.491	0.509	0.004347 0.004362					
			0.004329	0.004346	0.004292	+0.26	0.59	0.41
16	0.546	0.454	0.004480 0.004300					
			0.004424					
			0.004343					
			0.004405	0.004390	0.004397	-0.10	0.65	0.35
32	0.637	0.363	0.004466 0.004419					
			0.004582					
			0.004476					
			0.004556	0.004500	0.004568	-1.55	0.72	0.28

TABLE IX.— $K_N$  FOUND,  $K_N$  CALCULATED,  $\alpha$ ,  $(1 - \alpha)$ , ERROR IN PER CENT., AND PER CENT. OF REACTION DUE TO IONS AND TO MOLECULES FOR LITHIUM ETHYLATE AND METHYL IODIDE AT 0°.

V.	$\alpha$	$1 - \alpha$	$K_N$ found.	Av. $K_N$	$K_N$ calc.	% error.	Per cent. of reaction due to ions:	Per cent. of reaction due to molecules:
							$K_i\alpha/K_N$	$K_m(1-\alpha)/K_N$
2	0.144	0.856	0.002420	0.002406	0.002440	-1.40	0.30	0.70
			0.002381					
			0.002411					
			0.002417					
			0.002425					
4	0.220	0.780	0.002728	0.002690	0.002690	0.0	0.42	0.58
			0.002678					
			0.002663					
			0.002696					
8	0.312	0.688	0.002971	0.002978	0.002991	-0.43	0.53	0.47
			0.002986					
16	0.409	0.591	0.003304	0.003322	0.003310	+0.36	0.64	0.36
			0.003423					
			0.003330					
			0.003231					
32	0.519	0.481	0.003665	0.003619	0.003668	-1.30	0.73	0.27
			0.003657					
			0.003536					

TABLE X.— $K_i$  AND  $K_m$  FOR SODIUM, POTASSIUM, AND LITHIUM ETHYLATES AND METHYL IODIDE AT 0°.

Sodium Ethylate.			Potassium Ethylate.			Lithium Ethylate.		
V.	$K_i$	$K_m$	V.	$K_i$	$K_m$	V.	$K_i$	$K_m$
1 : 2	0.004598	0.003074	4 : 8	0.00543	0.00320	2 : 4	0.005590	0.001872
1 : 4	0.004883	0.003010	4 : 32/3	0.00562	0.00310	2 : 8	0.005317	0.001918
1 : 8	0.004896	0.003027	4 : 16	0.00528	0.00329	2 : 16	0.005360	0.001911
1 : 16	0.004878	0.003030	4 : 32	0.00513	0.00340	2 : 32	0.005174	0.001942
1 : 32	0.004824	0.003038	16/3 : 32/3	0.00564	0.00306	4 : 8	0.005134	0.002001
2 : 4	0.005109	0.002915	16/3 : 16	0.00522	0.00335	4 : 16	0.005297	0.001955
2 : 8	0.004995	0.002950	16/3 : 32	0.00508	0.00348	4 : 32	0.005115	0.002006
2 : 16	0.004930	0.002970	8 : 16	0.00517	0.00345	8 : 16	0.005411	0.001875
2 : 32	0.004849	0.002995	8 : 32	0.00502	0.00359	8 : 32	0.005109	0.002012
4 : 8	0.004914	0.003014	16 : 32	0.00493	0.00377	16 : 32	0.004922	0.002214
4 : 16	0.004874	0.003033						
4 : 32	0.004808	0.003066						
8 : 16	0.004846	0.003065						
8 : 32	0.004778	0.003116						
16 : 32	0.004737	0.003188						
Av.,	0.00486	0.00303		0.00525	0.00337		0.00524	0.00197
Dr. W. A. Taylor's								
Av.,	0.00496	0.00294						

Tests with a Beckmann thermometer showed that all parts of the bath remained within a few thousandths of a degree of zero. The ethylate solutions were made up at 0°, and transferred at this temperature into the

reaction flasks by surrounding the pipet with a jacket containing cracked ice and water. Ice-water from the bath was run continuously through the jacket of the machine by means of a pump run by a small electric motor. Although the exposed circulation was made as short as possible, the temperature of the water returning to the bath had risen several degrees. Even when this current of water was returned to the bath in the vicinity of the thermometer, no change in the temperature could be detected unless the water played directly upon the thermometer. In that part of the bath which contained the reaction flasks, no change in temperature could be detected. The delivery tube of the machine and all exposed connecting tubes were protected by several layers of binding tape, and that liquid in the most exposed part of the delivery tip was discarded just before each 10 cc. portion was run out. The reaction flask containing the ethylate solution was lifted from the bath in a beaker containing cracked ice and water, and after the alkyl halide solution had been transferred to it, the flask was returned to the bath as rapidly as possible. Tests made with the thermometer showed that by this method the temperature was kept below 0.5°, and the zero point was quickly reached by shaking the flask two minutes in the bath. For the work with the *N*/16 and *N*/32 solutions 40 cc. portions were used instead of the usual 20 cc., and the solutions were mixed by inverting and shaking the flasks under the ice-water. The corks were protected by rubber fingers over the necks of the flasks. A rise in the temperature of even several tenths of a degree for one minute would have but little effect on the constants, especially those for the dilute solutions for which the time periods were so long.

#### Summary.

1. It was shown how to purify and analyze methyl iodide. A number of samples boiled at about 42.35° and contained not over 0.05% impurities.
2. Special apparatus and baths for work at 0° are described.
3. The rates of a large number of reactions between methyl iodide and sodium, potassium, and lithium ethylates at 0° were studied. The concentration of the ethylates ranged from *N*/1 to *N*/32.
4. When the reaction velocities  $K_N$  and the ionization  $\alpha$  for the different concentrations for any given ethylate are substituted in the equation  $K_N = K_i\alpha + K_m(1 - \alpha)$  good constants are obtained for  $K_i$  and  $K_m$ .
5. The activity  $K_i$  of unit concentrations of the ethylate ion should be, and is, the same whether sodium, potassium, or lithium ethylate be employed, and averages about 0.0051 at 0°.
6. Since the nonionized molecules of sodium, potassium, or lithium ethylate are different substances, the values of  $K_m$  vary with the ethylate. For sodium ethylate it is about 0.0030, for potassium ethylate it is about 0.0034, and for lithium ethylate it is about 0.0020.
7. Since these solutions are concentrated and not ideal, the physical

constants such as viscosity, specific gravity, dielectric constant, refractive index,  $\alpha$ ,  $K_V$ , etc., are modified by the different substances present and corrections must be applied later to the data presented here. Only in this way can we obtain the final data freed from all normal and abnormal salt and solvent effects. It is believed from data obtained by adding some of these substances that these corrections will not be large enough to modify the general theory of the activity of both the ions and molecules of acids, bases, and salts.

JOHNS HOPKINS UNIVERSITY,  
June, 1913.

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[CHEMICAL SECTION, IOWA AGRICULTURAL EXPERIMENT STATION.]

## A COMPARISON OF BARBITURIC ACID, THIOBARBITURIC ACID AND MALONYLGUANIDINE AS QUANTITATIVE PRECIPITANTS FOR FURFURAL.

BY ARTHUR W. DOX AND G. P. PLAISANCE.

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All of the methods for the quantitative determination of pentoses and pentosans in agricultural products are based upon the conversion of pentose into furfural by distillation with a mineral acid, preferably hydrochloric, and subsequent estimation of furfural in the distillate by means of a suitable reagent. Günther, Chalmot and Tollens<sup>1</sup> titrated the furfural with phenylhydrazine, using aniline acetate paper as an indicator. Stone<sup>2</sup> made use of the same reaction, but used Fehling's solution to determine the excess of phenylhydrazine. Later, Flint and Tollens<sup>3</sup> showed that this titration method was not accurate, on account of the levulinic acid resulting from the decomposition of hexoses, as well as the instability of the standard phenylhydrazine acetate reagent used. Jolles<sup>4</sup> titrated the furfural with potassium bisulfite and iodine. In the absence of other reducing substances, the furfural could be determined directly with Fehling's solution. Günther and Tollens<sup>5</sup> precipitated the furfural as hydrofurfuralimide by means of ammonia, while Chalmot and Tollens<sup>6</sup> used phenylhydrazine and weighed the resulting hydrazone. In both cases the condensation product was somewhat soluble.

Councilor<sup>7</sup> was the first to use phloroglucinol for the quantitative determination of furfural. This method was later studied and perfected by Tollens and his co-workers. The phloroglucinol method, although

<sup>1</sup> *Ber.*, 24, 3577 (1891).

<sup>2</sup> *Ibid.*, 24, 3019 (1891).

<sup>3</sup> *Ibid.*, 25, 2912 (1892).

<sup>4</sup> *Ibid.*, 39, 96 (1906).

<sup>5</sup> *Ibid.*, 23, 1751 (1890).

<sup>6</sup> *Ibid.*, 24, 694 (1891).

<sup>7</sup> *Chem. Ztg.*, 17, 1743.

known to be faulty in several respects, is the one in general use to-day, having been adopted as provisional by the Association of Official Agricultural Chemists.<sup>1</sup> It is strictly empirical, since the nature of the reaction and the constitution of the condensation product have not been determined. Kröber<sup>2</sup> compiled a table in which the weight of furfural-phloroglucide obtained is interpreted in terms of furfural, xylose, arabinose or pentose. This table is purely empirical, being based on trial distillations and precipitations of the furfural, or the particular pentose employed, and not upon the molecular weight of the condensation product. Furthermore, this method calls for solubility corrections. Kröber assumes that two molecules of water are split out in the reaction between furfural and phloroglucinol. Goodwin and Tollens<sup>3</sup> claim that only one molecule of water is liberated at ordinary temperature, but if the reaction is carried out at a temperature of 80° three molecules are liberated. A slight variation in the conditions may, therefore, affect the result considerably. Kröber noted the fact also that when the phloroglucide is allowed to stand in the air for a time, it takes up moisture which cannot be expelled by subsequent drying. From this brief survey of the literature, it is obvious that the phloroglucinol method in common use is not altogether satisfactory.

Other reagents have also been tried with varying success. Kerp and Unger<sup>4</sup> used semioxamizine as a precipitant for furfural, but obtained results that were too low. Conrad and Reinbach<sup>5</sup> found that furfural and barbituric acid condensed in the presence of dilute hydrochloric acid. Subsequently, Unger and Jäger<sup>6</sup> applied this reaction to the quantitative determination of furfural. They found that six to eight times as much barbituric acid as the theory required was needed to give the calculated value for furfural. The condensation product had the advantage of being only very slightly soluble in hydrochloric acid (1.22 mg. per 100 cc.). They claim that barbituric acid does not precipitate the furfural derivatives of hexose origin and that these merely tend to color the solution yellow. The reaction is a very simple one, consisting in the condensation of one molecule of furfural and one molecule of barbituric acid, through the aldehyde group of the former and the methylene group of the latter, with the splitting out of one molecule of water. The product was found to contain 13.75% nitrogen, which is in close agreement with the calculated value of 13.63%. When prepared from the furfural distillate from natural sources, the product was found to contain 13.96% nitrogen.

<sup>1</sup> Bureau of Chem., *Bull.* 107, 54 (1905).

<sup>2</sup> *J. Landw.*, 48, 357.

<sup>3</sup> *Ber.*, 37, 315 (1904).

<sup>4</sup> *Ibid.*, 30, 590 (1897).

<sup>5</sup> *Ibid.*, 34, 1339 (1901).

<sup>6</sup> *Ibid.*, 35, 4440 (1902); 36, 1222 (1903).

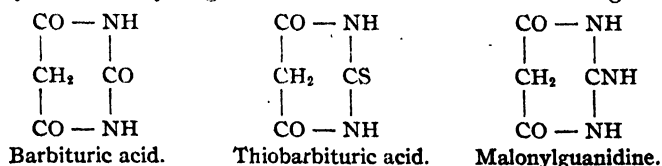
Fromherz<sup>1</sup> used barbituric acid as a precipitant for methyl furfural and found the condensation product to be not appreciably soluble. Fallada, Stein and Ravinka<sup>2</sup> found that barbituric acid and phloroglucinol gave very nearly the same results when pure xylose and arabinose were distilled and precipitated. On the other hand, when sucrose was added to the pentose, the results were very much higher when phloroglucinol was used as a precipitant than when barbituric acid was employed, the latter giving normal values. This substantiates the statements of other workers who found that hydroxymethylfurfural was not precipitated by barbituric acid.

The barbituric acid method possesses, therefore, certain advantages over the phloroglucinol method, in that the reaction is more specific and a definite condensation product is formed. The precipitate, however, is sufficiently soluble to render a solubility correction necessary. Then again, a large excess of the reagent appears to be necessary, indicating that possibly an occlusion of the precipitant leads to a compensation of errors.

The possibility of obtaining better results by using some derivative of barbituric acid will be discussed in the experimental part of this paper.

### Experimental.

Barbituric acid is ordinarily prepared by the condensation of urea with the sodium salt of malonic ester. The corresponding thio derivative was prepared by Michael,<sup>3</sup> and by Gabriel and Colmann<sup>4</sup> by condensing thio-urea with sodium malonic ester, and the imino derivative was prepared by Michael<sup>5</sup> and by Traube<sup>6</sup> from guanidine and malonic ester. These two derivatives are analogous in many respects to barbituric acid, as will readily be seen by a glance at the structural formulas given below.



It remained to be determined whether they would react in a similar manner with furfural, and possibly give a more complete precipitation.

The barbituric acid used in this work was a Kahlbaum preparation, which we purified further by recrystallization from water. Analysis showed it to contain 21.80% nitrogen; theory, 21.87%.

Our first preparation of thiobarbituric acid was made according to

<sup>1</sup> *Z. physiol. Chem.*, **50**, 241 (1910).

<sup>2</sup> *Oesterr.-ung. Z. Zuckerind.*, **43**, 425.

<sup>3</sup> *J. prakt. Chem.*, **35**, 456 (1887); **49**, 37 (1894).

<sup>4</sup> *Ber.*, **37**, 3657 (1904).

<sup>5</sup> *Loc. cit.*

<sup>6</sup> *Ber.*, **26**, 2553 (1893).

the method of Gabriel and Colmann. 2.3 g. of sodium were dissolved in 50 cc. absolute alcohol, and 16 g. malonic ester added, then 7.6 g. dry thiourea, previously dissolved in absolute alcohol. The mixture was heated on a water bath for ten hours. The white pasty mass which resulted was then treated with 80 cc. water and 7.6 cc. hydrochloric acid and gently warmed until it had dissolved. Upon standing, thiobarbituric acid crystallized out. The yield was about 30% of the theory. In preparing a further quantity of thiobarbituric acid we found that a much better yield was obtained when less solvent was used and the mixture heated for 15 hours in a sealed tube at 105° with twice the theoretical amount of sodium, as recommended by Fischer and Diltney<sup>1</sup> in their preparation of methylethyl- and dimethylthiobarbituric acid. The product, after acidifying with hydrochloric acid, was a slightly yellowish crystalline powder containing 19.61% nitrogen, whereas the theory calls for 19.45%. The yield in this case was 45% of the theory.

Malonylguanidine was made according to Traube from free guanidine and malonic ester. The condensation took place readily and gave an excellent yield. The product was used directly without further purification. It contained 32.71% nitrogen; theory, 33.06%.

Parallel determinations were now conducted, using barbituric acid (malonylurea), thiobarbituric acid (malonylthiourea) and malonylguanidine as precipitants for furfural. For this work a stock solution of pure, freshly distilled furfural of exactly 1% strength was prepared, and a 5 cc. aliquot taken for each determination. The furfural was diluted with 12% hydrochloric acid and solutions of the different precipitants in 12% hydrochloric acid added, the total volume of the reaction mixture being 400 cc. The conditions were, therefore, similar to those obtaining in pentosan determinations. Unless otherwise indicated, a slight excess of the precipitant was employed, the reaction carried out at room temperature, and the precipitate allowed to stand overnight before filtering on Gooch crucibles and drying to constant weight at 100°. The analytical results are set forth in the following tables.

From Table I it is at once apparent that the results with barbituric acid are uniformly low. The last three determinations show the effect of increasing amounts of the precipitant. With barbituric acid and furfural in molecular proportions of sixteen to one, the result is nearly quantitative. This observation is in accord with the statement of Unger and Jäger that eight times the theoretical amount of barbituric acid is necessary for complete recovery of the furfural.

With thiobarbituric acid, as shown in the table, the precipitation is quantitative without using a large excess of the reagent. The results

<sup>1</sup> *Ann.*, 335, 350 (1904).

tend even to run just a trifle over the theory. The last two determinations show that the reaction should not be allowed to occur at a high temperature, since this leads to results that are too low.

TABLE I.

Barbituric acid.				Thiobarbituric acid.			Malonylguanidine.		
Gram furfural taken.	Wt. of precipitate.	Gram furfural calculated.	Furfural recovered. %.	Wt. of precipitate.	Gram furfural calculated.	Furfural recovered. %.	Wt. of precipitate.	Gram furfural calculated.	Furfural recovered. %.
0.0583	0.1180	0.0550	94.3	0.1351	0.0584	100.2	0.0649	0.0305	52.3
0.0583	0.1180	0.0550 <sup>2</sup>	94.3	0.1360	0.0588	100.8	0.0640	0.0300	51.5
0.0583	0.1171	0.0546 <sup>2</sup>	93.6	0.1372	0.0593	101.7	0.0666 <sup>6</sup>	0.0031	12.7
0.0583	0.1174	0.0547 <sup>2</sup>	93.8	0.1367	0.0591	101.4	0.0035 <sup>6</sup>	0.0016	6.6
0.0583	0.0976	0.0455 <sup>1</sup>	78.0	0.1361	0.0588	100.8	0.0577	0.0270	46.3
0.0583	0.1194	0.0556 <sup>2</sup>	95.4	0.1368	0.0591	101.4	0.0610	0.0286	50.9
0.0583	0.1238	0.0580 <sup>3</sup>	99.5	0.1271 <sup>4</sup>	0.0550	94.3			
				0.1294 <sup>4</sup>	0.0559	95.9			

The condensation of furfural with malonylguanidine is not quantitative. The best yield in the determinations quoted above was only a little more than half the theory, hence under these conditions, malonylguanidine is not applicable for the quantitative determination of furfural.

Having shown that thiobarbituric acid in moderate excess gives quantitative results under the conditions of the above experiments, whereas barbituric acid under the same conditions gives less than 95% of the theoretical yield, it remains to compare these two reagents as regards their sensitiveness to smaller amounts of furfural. In the determinations recorded in Table II, four times the theoretical amount of barbituric acid was used.

TABLE II.—BARBITURIC ACID.

Gram furfural taken.	Wt. of precipitate.	Gram furfural calculated.	Error. Mg.	Furfural recovered. %.
0.0117	None	None	No ppt.	None
0.0117	0.0061	0.0028	— 8.9	26.5
0.0233	0.0225	0.0105	—12.8	45.6
0.0233	0.0334	0.0156	— 7.7	67.0
0.0350	0.0475	0.0221	—12.9	63.1
0.0350	0.0640	0.0298	— 5.2	85.1

It is obvious, therefore, that the barbituric acid method is inapplicable to the determination of small quantities of furfural.

In Table III, varying amounts of furfural are treated with varying amounts of thiobarbituric acid.

<sup>1</sup> Precipitated with a little more than the theoretical amount of barbituric acid.

<sup>2</sup> Precipitated with 4 times the theoretical amount of barbituric acid.

<sup>3</sup> Precipitated with 16 times the theoretical amount of barbituric acid.

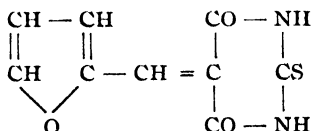
<sup>4</sup> Precipitated at 60°.

<sup>6</sup> 0.0244 g. furfural taken.



Gram furfural taken.	Gram thiobar- bituric acid taken.	Wt. of pre- cipitate.	Gram furfural calculated.	Furfural recov- ered. %.	Gram furfural taken.	Gram thiobar- bituric acid taken.	Wt. of pre- cipitate.	Gram furfural calculated.	Furfural recov- ered. %.
0.0592	0.18	0.1369	0.0592	100.0	0.0244	0.08	0.0568	0.0247	101.2
0.0592	0.18	0.1398	0.0603	101.8	0.0244	0.08	0.0560	0.0243	99.6
0.0592	0.18	0.1370	0.0592	100.0	0.0244	0.06	0.0556	0.0240	98.3
0.0592	0.18	0.1400	0.0605	102.3	0.0244	0.16	0.0573	0.0248	101.6
0.0592	0.12	0.1390	0.0601	101.6	0.0119	0.04	0.0277	0.0120	100.8
0.0592	0.12	0.1400	0.0605	102.3	0.0119	0.04	0.0275	0.0119	100.0
0.0592	0.20	0.1372	0.0593	100.2	0.0119	0.03	0.0261	0.0113	95.0
0.0360	0.11	0.0835	0.0361	100.3	0.0119	0.08	0.0278	0.0120	100.8
0.0360	0.11	0.0852	0.0369	102.5					

	Nitrogen.		Sulfur.	
	Found. %.	Calculated. %.	Found. %.	Calculated. %.
Furfuralmalonylurea . . . . .	13.60	13.65	.....	.....
Furfuralmalonylthiourea . . . . .	12.61	12.61	14.47	14.41
Furfuralmalonylguanidine . . . . .	15.61	16.01	.....	.....



The furfuralmalonylurea is a bright lemon-yellow, somewhat granular, precipitate which settles readily. Furfuralmalonylthiourea is also a brilliant lemon-yellow precipitate but very flocculent and voluminous. No difficulty was experienced in filtering and washing it, although the filtration was somewhat slow. It was practically insoluble in cold dilute mineral acids and only slightly soluble in hot acids. It was practically insoluble in alcohol, ether, petroleum ether, methyl alcohol, acetic acid, benzene, carbon disulfide and turpentine. In ammonia, pyridine and caustic alkalies it dissolves with ease, giving at first a greenish blue solution which gradually loses its color. From the alkaline solution it can be recovered by neutralizing with acid. The filtrates from both the furfuralmalonylurea and the furfuralmalonylthiourea had a very slight tinge of

yellow. Furfuralmalonylguanidine, on the other hand, is a very dark green, flocculent precipitate, appreciably soluble in hydrochloric acid. The filtrate is an intense greenish brown.

It was early noted that unless the thiobarbituric acid was carefully purified, the precipitation of furfural was not complete, only 90 to 95% of the latter being recovered, and the filtrate possessed a red color or sometimes a green color. In one set of determinations the difficulty was traced with reasonable certainty to the presence of cyanacetic ester in the malonic ester from which the thiobarbituric acid was made. In preparing malonic ester from chloroacetic acid in the usual way, some cyanacetic ester is apt to remain unless precautions are taken to carry the saponification to completion. This is difficult to separate from the malonic ester because the boiling points of the two substances lie only a few degrees apart. The cyanacetic ester in all probability reacts with the thiourea forming a di-cyandiacylthiourea. On fractional crystallization of one of our impure preparations of thiobarbituric acid, white needle shaped crystals were obtained, which on analysis yielded 26.66% nitrogen; calculated for di-cyandiacylthiourea, 26.65% nitrogen. These crystals when dissolved in 12% hydrochloric acid gave an intensely green precipitate with furfural, just as did the thiobarbituric acid before purification. For the preparation of thiobarbituric acid it is, therefore, recommended that the malonic ester be subjected to a repetition of the simultaneous saponification and esterification before condensation with thiourea, and that the thiobarbituric acid be purified by one or two crystallizations of its sodium salt.

**Methylfurfural.**—Methylpentosans often accompany the pentosans commonly found in plant structures. On hydrolysis they yield a methylpentose, usually rhamnose or fucose, and this on distillation with mineral acid is converted into methylfurfural which closely resembles furfural in most of its properties. Qualitatively, methylfurfural may be distinguished from furfural by the color reaction with aniline acetate which in this case is yellow instead of red.<sup>1</sup> When, however, furfural greatly predominates in the mixture, as is usually the case, the color test is not conclusive. Methylfurfural is precipitated by the same reagents which precipitate furfural, for example—phloroglucinol<sup>2</sup> and barbituric acid.<sup>3</sup> Ishida and Tollens<sup>4</sup> make use of the difference in solubility of the phloroglucides in alcohol for quantitative determinations, the loss in weight after extraction with alcohol being taken as representing the amount of methylfurfural phloroglucide. We have not been able to obtain satisfactory results by this method. For example, the phloroglucide prepared from pure furfural

<sup>1</sup> de Chalmot, *Am. Chem. J.*, 15, 278 (1893).

<sup>2</sup> Votocek, *Ber.*, 30, 1195 (1897).

<sup>3</sup> Fromherz, *loc. cit.*

<sup>4</sup> *J. Landw.*, 1911, 70.

was appreciably soluble when subjected to continuous extraction with alcohol. At the same time the insoluble residue sometimes increased in weight during this operation. The loss in weight and the direct weight of the extracted material seldom agreed, the difference running as high as 25 mg.

Pure methylfurfural could not be obtained from the chemical supply houses or from other institutions, and the amount of rhamnose at our disposal was very limited, hence the reaction could not be carried out quantitatively with definite amounts as was done in our previous work with furfural. In the few experiments which we were able to carry out with methylfurfural, the distillate obtained by distilling rhamnose with 20% sulfuric acid was used. This was made 12% acid with hydrochloric acid and treated with thiobarbituric acid as already described. A flocculent yellow precipitate resulted, which closely resembled the corresponding furfural derivative, and showed practically the same solubilities as the latter. The filtrate was only slightly colored and gave no reaction with aniline acetate paper.

Calc. for  $C_{10}H_8N_2O_3S$ : N, 11.86%; S, 13.56%. Found: N, 11.91; S, 13.50.

It will be noted that methylfurfuralmalonylthiourea contains only 0.75% less nitrogen than furfuralmalonylthiourea. Owing to the relatively large size of the molecule, the introduction of a single methyl group makes only a slight difference in the percentage composition. The presence of methylfurfural in the proportion of one to three of furfural could undoubtedly be detected by analysis of the thiobarbituric acid condensation product. In mixtures where the ratio is less than one to four the lowering of the nitrogen content would be within the limit of analytical error, and hence inconclusive as evidence of the presence of methylfurfural.

### Discussion.

Our experiments, quoted above, show that thiobarbituric acid condenses readily with furfural in the presence of 12% hydrochloric acid. The reaction is quantitative, giving a voluminous precipitate which can be filtered, dried and weighed. As a precipitant for furfural, thiobarbituric acid is superior to phloroglucinol, in that no correction for solubility of the product is necessary. It is also preferable to barbituric acid for the reason that the reaction is quantitative with as small amounts of furfural as 12 mg. and a large excess of the precipitant is not necessary, thus avoiding possible errors due to inclusion. Unlike the phloroglucinol product, the resulting furfurylmalonylthiourea is a definite substance resulting from the condensation of one molecule of furfural with one molecule of thiobarbituric acid by the elimination of one molecule of water, and a definite chemical formula can be assigned to it. It has a further advantage in that the percentages of nitrogen and sulfur, which agree with those

calculated from the formula, can be determined by analysis and used as a positive means of identification of the product to distinguish it from, or detect the presence of similar products which might result in case homologs of furfural were present. For example, if a mixture of furfural and sufficient methylfurfural were precipitated, the determinations of nitrogen and sulfur on the product should enable us to compute the relative amounts of these two aldehydes, and, therefore, the relative amounts of pentosans and methylpentosans in the original sample. At present the only means of estimating separately the furfural and methylfurfural present in a mixture such as is frequently met with in analysis, is the supposed differential solubility of their phloroglucides in alcohol, and this is admittedly unreliable.

It is suggested that thiobarbituric acid, which is not difficult to prepare in a pure state, may be found useful in the analysis of agricultural products, in place of phloroglucinol or barbituric acid, for the determination of pentoses and pentosans.

AMES, IOWA.

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[CONTRIBUTION FROM THE CHEMICAL SECTION, IOWA STATE COLLEGE.]

## CONDENSATION OF THIOBARBITURIC ACID WITH AROMATIC ALDEHYDES.

BY ARTHUR W. DOX AND G. P. PLAISANCE.

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The condensation occurring between aldehydes and the methylene group of malonic acid or its ester is well known. Less known, however, is the fact that the same reaction can be made to occur between aldehydes and the ureides of malonic acid. Conrad and Reinbach<sup>1</sup> condensed malonylurea (barbituric acid) with benzaldehyde, salicylaldehyde, *o*-nitrobenzaldehyde, *o*-aminobenzaldehyde, cinnamic aldehyde, and furfural. The reaction was carried out in aqueous solution at the temperature of the water bath. Salicylic aldehyde condensed with two molecules of barbituric acid, but in every other instance the condensation was in equimolecular proportions. Weinschenk<sup>2</sup> condensed barbituric acid with *p*-hydroxybenzaldehyde and with *p*-dimethylaminobenzaldehyde, heating the mixtures with alcohol on the water bath. Later, Whiteley<sup>3</sup> condensed 1,3-diphenylbarbituric acid with benzaldehyde and with cinnamic aldehyde, by heating with alcohol under a reflux. The same reaction was subsequently carried out by Whiteley and Mountain,<sup>4</sup> using 1,3-diphenylthiobarbituric acid. Jäger and Unger<sup>5</sup> found that in the pres-

<sup>1</sup> *Ber.*, **34**, 1339 (1900).

<sup>2</sup> *Ibid.*, **34**, 1685 (1900).

<sup>3</sup> *J. Chem. Soc.*, **91**, 1330 (1907).

<sup>4</sup> *Proc. Chem. Soc.*, **25**, 121 (1909).

<sup>5</sup> *Ber.*, **35**, 4440 (1902).

ence of 12% hydrochloric acid, barbituric acid and furfural condense quantitatively in the cold. This reaction has been applied by the writers<sup>1</sup> to the condensation of thiobarbituric acid with furfural and methylfurfural as a quantitative method for furfural in preference to the barbituric acid method. The two resulting products, furfuralmalonylthiourea and methylfurfuralmalonylthiourea, have been described in a previous paper.

In the present paper this reaction has been extended to other aromatic aldehydes and a number of new derivatives are here described.

**Benzalmalonylthiourea.**—Molecular proportions of benzaldehyde and thiobarbituric acid were dissolved in 12% hydrochloric acid and the solutions mixed. A lemon yellow precipitate at once formed. After standing a few moments, it was filtered, washed thoroughly with hot water, and finally with alcohol and ether. The product was only slightly soluble in alcohol and glacial acetic acid, but readily soluble in pyridine and in caustic alkalies. In ether, petroleum ether, benzene and carbon disulfide it was practically insoluble.

Calc. for  $C_6H_5CH : C_4H_2O_2N_2S$ : N, 12.07%; S, 13.79%. Found: N, 12.19; S, 13.71.

**o-Hydroxybenzalmalonylthiourea.**—Salicylaldehyde and thiobarbituric acid in 12% hydrochloric acid reacted in like manner, giving an immediate precipitation of a bright vermilion colored product. It showed the same solubilities as the corresponding product previously described. With dilute ammonia or caustic alkalies it gave a deep wine red color which rapidly disappeared.

Calc. for  $HO.C_6H_4.CH : C_4H_2O_2N_2S$ : N, 11.30%; S, 12.94%. Found: N, 11.41; S, 12.61.

**o-Nitrobenzalmalonylthiourea.**—Under the above conditions, nitrobenzaldehyde gave a greenish yellow product, with the same solubilities.

Calc. for  $NO_2.C_6H_4.CH : C_4H_2O_2N_2S$ : N, 15.00%; S, 11.55%. Found: N, 15.07; S, 11.29.

**p-Methoxybenzalmalonylthiourea.**—With anisic aldehyde and thiobarbituric acid, the product was a deep yellow precipitate, insoluble in the usual solvents except alkalies.

Calc. for  $CH_3O.C_6H_4.CH : C_4H_2O_2N_2S$ : N, 10.70%; S, 12.21%. Found: N, 10.58; S, 12.05.

**3-Methoxy-4-hydroxybenzalmalonylthiourea**—Vanillin condensed readily with thiobarbituric acid, giving a brilliant orange colored precipitate. In caustic alkalies the product gave a mahogany red solution, but the color rapidly faded.

Calc. for  $(CH_3O)(HO)C_6H_3.CH : C_4H_2O_2N_2S$ : N, 10.07%; S, 11.87%. Found: N, 10.05; S, 11.79.

**3,4-Methylenedioxybenzalmalonylthiourea.**—In the same manner piperonal condensed with thiobarbituric acid, with the formation of a bright orange colored precipitate, soluble only in alkalies.

<sup>1</sup> THIS JOURNAL, 38, 2156 (1916).

Calc. for  $\text{CH}_3\text{O}_2 = \text{C}_6\text{H}_5\text{CH}:\text{C}_6\text{H}_5\text{O}_2\text{N}_2\text{S}$ : N, 12.07%; S, 13.79%. Found: N, 12.19; S, 13.71.

**3,5-Dihydroxyphthalaldimalonylthiourea.**—Resorcinoldialdehyde condensed with two molecules of thiobarbituric acid. The product was a reddish brown precipitate, soluble in alkalis, to a mahogany red solution.

Calc. for  $(\text{HO})_2\text{C}_6\text{H}_2(\text{CH})_2 (= \text{C}_6\text{H}_5\text{O}_2\text{N}_2\text{S})_2$ : N, 13.40%; S, 15.40%. Found: N, 13.90; S, 15.50.

**Cinnamylidenemalonylthiourea.**—Cinnamic aldehyde yielded with thiobarbituric acid a bright orange red precipitate, soluble only in alkalis.

Calc. for  $\text{C}_6\text{H}_5\text{CH}:\text{CHCH}:\text{C}_6\text{H}_5\text{O}_2\text{N}_2\text{S}$ : N, 10.85%; S, 12.40%. Found: N, 10.69; S, 12.15.

None of the substances described above could be melted without decomposition. The temperatures at which decomposition and charring began varied from  $220^\circ$  to  $300^\circ$ , but in no case was the decomposition temperature sufficiently sharp to serve as a means of identification. It is of interest to note that the condensation products of thiobarbituric acid with the three aldehydes which contain a hydroxyl group on the benzene nucleus gave a deep red coloration with caustic alkalis, while the others remained colorless under this treatment. In all cases the yield was practically quantitative.

The precipitation of aromatic aldehydes by thiobarbituric acid in the presence of 12% hydrochloric acid appears to be a general reaction. The products all have an intense yellow or yellowish red color. Three aliphatic aldehydes tried—formaldehyde, acetaldehyde and citral—failed to react under these conditions.

AMES, IOWA.

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[CONTRIBUTION FROM THE SYNTHETIC PRODUCTS LABORATORY OF THE BUREAU OF CHEMISTRY.]

## RESEARCHES ON ORGANIC PERIODIDES.

### II. PERIODIDES OF ANTIPYRINE, IODOANTIPYRINE AND PYRAMIDONE.

By W. O. EMERY AND S. PALKIN.

Received August 9, 1916.

#### Introduction.

The earliest available record of the action of iodine on antipyrine is that of Manseau,<sup>1</sup> who found that in aqueous solution and in the absence of free acid a relatively small but constant quantity of iodine was absorbed, which behavior he proposed to utilize as a basis for the proximate assay of antipyrine. Beyond noting the fact that apparent substitution took place until a point was reached when further addition of iodine produced a tarry precipitate, no attempt was made to ascertain the nature of the reaction or of the compounds formed. From a quantita-

<sup>1</sup> *Bull. soc. pharm. Bordeaux*, 1889, 148.

tive standpoint, better results were obtained by Schuyten,<sup>1</sup> who titrated very small amounts of antipyrine in relatively large volumes of water with an aqueous solution of iodine. Clearer insight into the mechanism of reaction between iodine and antipyrine is afforded by the work of Bougault,<sup>2</sup> who caused these two substances to react in alcoholic solution and in the presence of mercuric chloride, thereby effecting an absorption of approximately 1 molecule of iodine for every molecule of antipyrine involved. It was further noted by this investigator that, when a neutral aqueous solution of antipyrine was treated with iodine and the liquid kept neutral or even slightly alkaline by an antiacid like sodium acetate, or better according to our own experience, sodium bicarbonate, reactions take place whereby primarily formed antipyrine diiodide splits off a molecule of hydriodic acid, with the result that an atom of hydrogen in antipyrine is replaced by an equivalent of iodine, thus yielding iodoantipyrine,  $C_{11}H_{11}N_2IO$ , identical with the substance first prepared by Dittmar<sup>3</sup> from antipyrine and iodinetrichloride. In fairly concentrated alcoholic or strongly mineral acid solutions, however, there is practically no substitution, hence it follows that in all operations looking to the formation of antipyrine periodides solely, careful attention must be paid to the nature and concentration of the solvent media employed.

In the course of an investigation designed to test the availability of Wagner's reagent (an aqueous solution of iodine and potassium iodide) in alkaloidal assay, Kippenberger<sup>4</sup> reported a method for estimating antipyrine based on the formation of a periodide. He found that when this reagent was added to a moderately concentrated solution of antipyrine in the presence of a mineral acid, a dark brown precipitate was formed, which, on shaking a few minutes, separated as a tarry uncrystallizable mass, leaving a clear supernatant liquid more or less colored with iodine. In the absence of any considerable excess of iodized potassium iodide, the separation proved to be quantitative, a fact we have made use of in the development of a recently published gravimetric method for the estimation of antipyrine.<sup>5</sup> According to Kippenberger's views, all the iodine of the tarry precipitate or periodide, to which he ascribed the composition,  $C_{11}H_{11}N_2O.HI.I_2$ , was derived solely from free iodine of the reagent, the hydriodic acid portion emanating from the interaction of free iodine with water, thus:  $2I + 2H_2O = 2HI + H_2O_2$ . This rather startling theory as viewed from the conditions of the experiment was very promptly attacked by Scholtz,<sup>6</sup> who, not satisfied with declaring the

<sup>1</sup> *Chem. Ztg.*, 19, 1786 (1895).

<sup>2</sup> *J. pharm. chim.*, [6] 7, 161 (1898); [6] 11, 98 (1900).

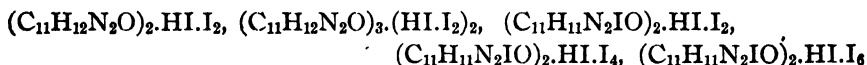
<sup>3</sup> *Ber.*, 18, 1617 (1885).

<sup>4</sup> *Z. anal. Chem.*, 35, 659 (1896).

<sup>5</sup> *J. Ind. Eng. Chem.*, 6, 751 (1914).

<sup>6</sup> *Arch. Pharm.*, 237, 71 (1899).

method worthless, pronounced the analytical results untrustworthy and the theory of the periodide formation untenable, whereupon a lengthy controversy ensued,<sup>1</sup> in the course of which Kippenberger, while admitting certain inaccuracies in his method, still insisted that the iodine of the hydriodic acid had its rise in free iodine itself. That Kippenberger obtained a tar of the above formula in certain definite concentrations of iodine, can hardly be questioned, but that a compound of the composition indicated always precipitates with only two "exterior" iodine atoms, irrespective of the quantity of iodine employed, was partly disproved by a number of experiments which he himself records, and we have ourselves obtained results fully substantiating the criticisms advanced by Scholtz and demonstrating beyond the possibility of doubt that Kippenberger's theory of periodide formation, in general, and his antipyrine method, in particular, are quite fallacious. As will presently appear from a presentation of experimental data, the unsightly tars ordinarily obtained by the action of iodine on antipyrine may consist of one or several periodides, of which we finally succeeded, after no little trouble and experimentation, in isolating and characterizing the following in crystalline form:



All attempts to prepare a crystalline periodide of the composition favored by Kippenberger yielded negative results.

With a view to clearer presentation, the experimental portion of this paper has been subdivided into: I. Behavior of antipyrine toward iodized potassium iodide, and composition of the resulting tars; II. Crystalline periodides of antipyrine; III. Crystalline periodides of iodoantipyrine; IV. Crystalline periodides of pyramidone.

### Experimental.

**Behavior of Antipyrine toward Iodized Potassium Iodide, and Composition of the Resulting Tars.**—In the following series of experiments, 10 cc. of a 1% solution of antipyrine were introduced into each of four 100 cc. volumetric flasks provided with glass stoppers, then treated with 40 cc. water and 30 cc. 0.965 *N*/20 iodine (equivalent to 28.95 cc. *N*/20 iodine). To the several flasks were thereupon added 2.5, 5, 10 and 12 cc. of concentrated hydrochloric acid (about 37%), respectively. After shaking for about five minutes, the liquid was diluted to 100 cc., again shaken to uniformity, then filtered through a funnel stoppered with glass wool overlaid with asbestos. A 50 cc. aliquot of the filtrate was titrated with sodium thiosulfate. Results of these experiments are set forth in tabulated form in Table I.

<sup>1</sup> *Z. anal. Chem.*, 38, 230, 278, 280 (1899); *Arch. Pharm.*, 238, 135, 301 (1900).



TABLE I.

	Antipyrine. Gram.	N/20 iodine. Cc.	Concd. HCl. Cc.	N/20 Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> for unexpended iodine in		N/20 iodine consumed. Cc.
				50 cc.	100 cc.	
1.....	0.1000	28.95	2.5	1.75	3.5	25.45
2.....	0.1000	28.95	5.0	1.90	3.8	25.10
3.....	0.1000	28.95	10.0	2.50	5.0	23.95
4.....	0.1000	28.95	12.0	3.35	6.7	22.25

Examination of the foregoing data shows that iodine consumption varied with changing amounts of acid, gradually decreasing with increasing concentration of acid, and furthermore that, even with the minimum expenditure of iodine, there was no absorption equivalent to two atoms of iodine per molecule of antipyrine, although an approach to that relationship is indicated. Thus, it will be noted that as the acid increased from 2.5 cc. to 12 cc., the consumed iodine fell from 25.45 to 22.25 cc. N/20 iodine. Theoretically, 0.1000 g. antipyrine would require 21.3 cc. N/20 iodine for the formation of a tar or periodide corresponding in composition to Kippenberger's formula.

Such results quite naturally led us to consider what effect, if any, varying quantities of iodine would have on iodine absorption, all other factors remaining constant. To this end, 0.1000 g. portions antipyrine were introduced into 100 cc. volumetric flasks, as in the first series of experiments, along with 5 cc. concentrated hydrochloric acid, the mixture diluted somewhat, and from about 30 to 80 cc. standard iodine added. After shaking until the solution was clear and diluting to mark, 50 cc. aliquots were taken as before and titrated with thiosulfate. The results are shown in Table II.

TABLE II.

	Antipyrine. Gram.	N/20 iodine. Cc.	HCl. Cc.	N/20 Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> for unexpended iodine in		N/20 I. Cc.	Atoms I consumed per mol antipyrine.
				50 cc.	100 cc.		
1.....	0.1000	28.95	5	2.05	4.1	24.85	2.33
2.....	0.1000	33.75	5	2.70	5.4	28.35	2.66
3.....	0.1000	38.60	5	3.50	7.0	31.60	2.97
4.....	0.1000	48.25	5	5.95	11.9	36.35	3.42
5.....	0.1000	67.60	5	12.80	25.6	42.00	3.95
6.....	0.1000	77.20	5	15.50	31.0	46.20	4.30
7.....	0.1000	77.20	5	16.40	32.8	44.40	4.17

From these results it is evident that increase in iodine concentration causes a marked increase in the quantity of iodine absorbed, Experiments 1-6 showing a range of 2.33 to 4.3 atoms of iodine per molecule of antipyrine. In order to ascertain what affect heat might have on the reaction, Expt. 7 was carried out—identical in every way with Expt. 6 except that the liquid was heated to 60°—with the result that apparently less iodine was consumed than when the reaction took place in the cold. This is contrary to what might have been expected and is perhaps due to loss of

iodine by volatilization rather than through difference in iodine absorbed or increased solubility of the tar in the reacting menstruum.

In the preceding experiments, conclusions relative to the nature of the tars produced were drawn solely from titrations of the unexpended iodine of the filtrates. In order to obtain a more direct index of the additive iodine content of the tar, estimations of halogen were made in the tarry residues themselves. The question naturally suggesting itself was whether all the iodine consumed in the operation was expended in the form of additive iodine for periodides and hence titratable, or whether some was used in other ways, notably in the formation of hydriodic acid or in direct substitution, whereby two atoms of iodine would be required for every atom substituted.

Accordingly, a series of experiments was run involving constant quantities of antipyrine in like concentrations of acid but varying volumes of *N*/20 iodine. The various operations of filtering and washing of the resultant tars were carried out in the manner already described, the aliquot portions of filtrates titrated with standard thiosulfate, while the tarry residue was dissolved in chloroform and titrated separately, being subjected to vigorous shaking in a glass-stoppered flask during titration to a complete discharge of color. The standard solutions were so adjusted that  $I^- = 0.0507 N = Na_2S_2O_3$ . The results are set forth in Table III.

TABLE III.

	Anti- pyrine. Gram.	HCl Cc.	<i>N</i> /20 iodine. Cc.	<i>N</i> /20 thio- sulfate. Cc.	Total I consumed. Cc.	Atoms I consumed per mol antip.	$Na_2S_2O_3$ required for tar. Cc.	Atoms I consumed per mol antip.	Iodine un- accounted for. Cc.
1	0.1	10	25	4.0	21.0	1.94	19.15	1.83	1.85
2	0.1	10	30	4.7	25.3	2.41	24.75	2.36	0.55
3	0.1	10	35	6.05	28.95	2.76	28.55	2.72	0.40
4	0.1	10	40	8.4	31.6	3.01	30.25	2.88	1.35
5	0.1	10	50	13.2	36.8	3.51	35.3	3.37	1.5
6	0.1	10	70	28.45	41.55	3.96	39.0	3.72	2.5
7	0.1	10	100	52.65	47.35	4.52	43.35	4.14	4.0
8 <sup>1</sup>	0.1	10	50	48.6	48.6				1.4
9 <sup>2</sup>	0.1	10	25	23.2	23.2				1.8

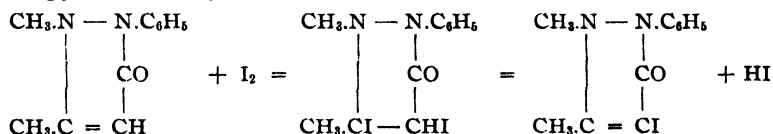
from which it appears that by far the greater portion of the expended iodine was present in titratable form, presumably in periodide combination, while a relatively smaller, yet variable, portion found application in other ways. Experiments 8 and 9 were carried out with a view of determining whether it would be possible under a somewhat modified treatment to realize a more nearly complete iodine recovery. To this end, chloroform was added to the flask after precipitation and the resulting mixture containing both the tar and unexpended iodine subjected to titration. Since the entire operation thus took place in the original closed

<sup>1</sup> Total supernatant liquid and tar titrated in original flask.

<sup>2</sup> As in the preceding, except that titration was effected after standing 2½ hours.

system, mechanical loss of iodine was reduced to a minimum. Even under such conditions, practically the same discrepancy was found to exist between the quantity of iodine applied and recovered as in Expts. 1 and 5. It will be noted that the "unaccounted for" iodine ranges from 0.4 to 4.0 cc. *N*/20, an equivalent of about 0.04 to 0.4 atom per molecule of antipyrine, or an average of not more than 0.16 atom of iodine per molecule. This apparent loss—comparable in a way with that observed by Holmes<sup>1</sup> in somewhat similar work on the alkaloids: morphine, codeine and heroine—is in the case of antipyrine unquestionably due to a secondary reaction amounting in the end to substitution, the chief controlling factors of which are concentration of iodine and of mineral acid.

If one examines the constitution of antipyrine—as exemplified in its generally accepted formula—with respect to the possibilities or extent of iodation, it will be seen that, aside from additive tendencies centering about the nitrogen atoms, the pyrazolone ring is made up of two double bonded carbon atoms, which under certain conditions readily unite with iodine to yield antipyrine diiodide, the latter subsequently passing into iodoantipyrine and hydriodic acid, thus:



a reaction, which in reality forms the basis of procedures already mentioned in the introduction and developed by Manseau, Schuyten and Bougault. Examination of the data obtained in the foregoing series of experiments will show that the limit of iodine addition was approximately four atoms to the molecule of antipyrine, since by the use of 100 cc. *N*/20 iodine to 0.1 g. antipyrine (equivalent to nearly ten atoms iodine (Expt. 7.)) there was actually present in the tar only slightly over four atoms (4.14, to be exact) in titratable form, although the total consumption amounted to 4.5 atoms per molecule. This, taken in conjunction with the fact that antipyrine is a monoacid base, might justify the assumption that the above cited treatment with iodine and hydriodic acid would yield an addition product of the formula:  $\text{C}_{11}\text{H}_{12}\text{N}_2\text{O} \cdot \text{HI} \cdot \text{I}_4$ , which of course in no way accounts for the molecular distribution of the added components. It might be stated in this connection, however, that any iodine expended in the saturation of double bonded carbon atoms could hardly be so loosely held as to react with thiosulfate in the ordinary course of titration; furthermore, the behavior of iodine in the formation of addition products with organic bases is generally quite irregular and without regard to nitrogen valence; finally, since the periodides of anti-

<sup>1</sup> *Phil. J. Sci.*, 6, 253 (1911).

pyrine as ordinarily obtained are noncrystalline tar-like masses, they may well, and doubtless do, act in the nature of solvents for iodine, beyond that required for addition products of definite composition. All such considerations, however, relative to the manner in which the iodine is actually consumed, would be of no great consequence from an analytical standpoint, provided a constant behavior could be assured, for the reason that the value of any method designed to secure quantitative results must necessarily depend on that feature.

### Conclusions.

When an aqueous-acid solution of antipyrine is treated with a solution of iodized potassium iodide in excess:

(1) The quantity of iodine consumed varies inversely with the amount of mineral acid present.

(2) The quantity of iodine consumed varies directly with its concentration.

(3) Two atoms of iodine per molecule of antipyrine, as found by Kippenberger, is not the limit of possible iodine consumption. On the contrary, the quantity of additive iodine corresponds more nearly to four atoms.

(4) Some iodine is expended in substitution, controlling factors of which are concentration of iodine and of mineral acid.

**Crystalline Periodides of Antipyrine.**—In Kippenberger's investigations on the so-called periodides of antipyrine, special mention was made that all efforts to obtain definite crystalline compounds from the various tars examined were futile. Manseau likewise merely noted the formation of a tarry precipitate on treating an acid solution of antipyrine with iodine in excess. Bougault<sup>1</sup> reported that when an alcoholic solution of antipyrine was treated with iodine there is formed an addition product which first precipitated in the form of a black oil but, on long standing, yielded needle-like aggregates with greenish reflection. These he claimed decomposed easily, dissociated in almost all solvents with liberation of free iodine, and, as a consequence, were not susceptible of isolation in a pure state. Further than the above, no attempts apparently have been recorded with a view to the preparation of antipyrine periodides of definite composition. A systematic investigation of the possible ways of obtaining such compounds involved not only experimentation with a large number of solvents and solvent mixtures, but also application of various solvents to each of a large number of periodides which in themselves differed widely in iodine content. In a general way it may be stated that the following facts were observed, affecting the solubility of most of the periodides examined: They are, for example, practically insoluble in cold aqueous acids; only very slightly soluble in petroleum ether (b. p. 30–60°) and

<sup>1</sup> *Loc. cit.*

carbon bisulfide; moderately soluble in cold, more so in hot ethyl acetate; very slightly soluble in cold ether, moderately soluble when warmed; quite soluble in all alcohols, more so in methyl than ethyl, and more in ethyl than amyl alcohol; chloroform is a very good solvent, while acetone is the best of all. From this it will be readily understood what an infinite field of possibilities opens up to the investigator who attempts an exhaustive study of all combinations of solvents, both pure and mixed, with the various periodide tars and under varying degrees of temperature. Nevertheless, a large number of experiments carried out in this field gradually forced the conviction that crystalline products could be best obtained by the use of organic solvents, of which alcohol, ether and ethyl acetate, yielded the most promising results. Thus, it was found possible, by the judicious application of the last mentioned solvent media—either singly or in admixture—to the tars themselves, to isolate three distinct periodides, derivatives of antipyrine.

For the sake of convenience and clearness it has been deemed expedient in a further presentation of the subject to divide the iodine addition products emanating from antipyrine itself into two general classes: (1) Periodides of antipyrine hydriodide, and (2) Periodides of iodoantipyrine hydriodide. Representatives of Class 1 were prepared in a more or less acid medium while those of Class 2 were isolated from media maintained quite neutral or slightly alkaline. Reference has already been made to certain principles underlying the conditions which inhibit or favor iodine substitution in the pyrazolone nucleus. Thus, the presence of a strong mineral acid or excess of an organic solvent such as alcohol, prevents substitution almost entirely, while carbonates, bicarbonates and even acetates of the alkali metals, as also diminution of the organic solvent (alcohol) by dilution with water, favor substitution to such a degree that with sufficient iodine available the reaction becomes complete as regards the eventual replacement of one hydrogen atom of the antipyrine by an equivalent of iodine. It should be noted, however, in this connection, that Class 1 differs further from Class 2 in that in the latter case an alkaline or neutral medium is maintained only until complete substitution has taken place, that is, until iodoantipyrine has been produced, the medium from there on being rendered acid, whereas in Class 1 the condition of the medium throughout the entire operation of periodide formation is one of acidity.

For the actual preparation of crystalline derivatives, two general methods naturally suggested themselves, either to prepare the indefinite tars by rapid precipitation in a medium in which they are quite insoluble (absence of organic solvent), followed by solution in a second medium more favorable to crystallization, or to bring together all the ingredients as antipyrine, hydriodic acid and iodine under conditions immediately

favorable to crystallization (organic solvents), thus entirely eliminating all intermediate steps for preparing the tar. As a matter of fact, the former method is the one which first yielded crystalline derivatives, and for a time at least it was found impossible to obtain them by any other treatment. Later, however, better success was had with the second and more direct procedure, purer products being obtained and far more expeditiously than with the earlier method. The second method will therefore be described exclusively in the preparation of the several compounds presently to be enumerated.

**Triantipyryne Dihydriodotet iodide,  $(C_{11}H_{12}N_2O)_3 \cdot (HI \cdot I_2)_2$ .**—This compound is readily obtained by dissolving its components: antipyryne, hydriodic acid and iodine in about equimolecular proportions in alcohol and allowing the resulting liquid to slowly deposit crystals. Thus, one sample was obtained in the following manner: 6.5 g. iodine were weighed out in a 50 cc. beaker and treated with a previously prepared solution of hydriodic acid<sup>1</sup> in alcohol in small portions, the mixture being stirred and subsequently decanted from any undissolved iodine into a 250 cc. beaker, until by this progressive treatment complete solution of iodine was effected. The iodized hydriodic acid was thereupon warmed to about 60° and slowly added with constant stirring to a warmed solution of 5 g. antipyryne in 20 cc. alcohol, the resulting liquid then diluted with a warmed mixture of 25 cc. alcohol and 25 cc. water, stirring the while, the beaker covered with a watch glass and set aside 24 hours. Slow crystallization favors the formation of large crystals, especially when the solution is seeded with one or more crystals. After standing the allotted time, the resulting product was filtered by suction through a small filter plate, the crystals thereupon returned to the beaker and washed several times by decantation with water, then subjected to renewed suction on the filter, dried in the air on filter paper, and finally in a desiccator until no odor of iodine could be detected. An additional crop of crystals can be obtained, either by chilling the alcoholic filtrate in a refrigerator or by slowly diluting same with a little warm water until the solution appears faintly turbid, then allowing to stand as before. This second treatment is not advocated, however, for the reason that the product resulting therefrom not infrequently shows an iodine content differing materially

<sup>1</sup> 6.7 g. potassium iodide were dissolved in the least possible quantity of water contained in a 50 cc. lipped Erlenmeyer flask, 4 cc. concentrated hydrochloric acid added, followed more gradually and with constant agitation with 20 cc. absolute alcohol. The liquid was made to pass through a small folded filter, or better through a small suction plate and filter, the filtrate and washings (two 10 cc. portions absolute alcohol) being in the latter event collected in a test tube contained in the suction Erlenmeyer flask. In the case where the ordinary folded filter was used, both filtrate and washings were collected in a second 50 cc. Erlenmeyer flask. This method will be found most convenient for the rapid preparation of alcoholic hydriodic acid,

from that of crystals first separating. Attention might properly be called at this point to the proportions in which the essential ingredients are employed, namely: 1 molecule of antipyrine, 2 atoms of iodine and 1 molecule of hydriodic acid, the purpose being to produce a compound of the same composition as the tarry substance described by Kippenberger and alleged to have the formula  $C_{11}H_{12}N_2O.HI.I_2$ . No such compound resulted, however, as will presently be shown by the analytical data obtained. The above cited proportions are susceptible of considerable variation, with some consequent change in the yield, but little or none in the composition of the resultant periodide. Crystals from repeated experiments were small to large steely blue needle-like prisms with metallic luster, odorless when perfectly dry, quite stable in the air and having no water of crystallization. They are extremely soluble in acetone, less so in chloroform, moderately soluble in methyl and ethyl alcohol, sparingly so in iodized potassium iodide solution, and quite insoluble in water. The specific gravity of these crystals was found to be 1.91, the melting point  $79-80^\circ$ . In determining the composition of the periodide, recourse was had to elementary analysis with respect to carbon, hydrogen and nitrogen, to the estimation of total and of "exterior" or additive iodine, as also of antipyrine itself.

Aside from complications incident to the presence of nitrogen, considerable difficulty was experienced in the carbon and hydrogen determinations, owing to the relatively high iodine content and its resistance to fixation. Extraordinary precautions were therefore necessary to provide against possible passage of this element into the absorption train. In spite of all safeguards, however, as interposition of silvered copper between the lead chromate and reduced copper spirals, sufficient iodine escaped to materially affect the values for carbon and hydrogen.

In the otherwise comparatively simple operation of determining iodine by titration with thiosulfate, numerous difficulties presented themselves. As previously pointed out, when antipyrine and iodine are brought together in a neutral or alkaline medium, conditions favorable to substitution at once obtain, so that by dissolving the periodide in alcohol, or other organic solvent, and adding aqueous thiosulfate, the tendency to such reaction becomes more and more pronounced, progressively so in fact with increasing quantities of the aqueous reagent, hence treatment under the conditions mentioned invariably yielded low values for iodine. Since the total consumption of this element is in quantity twice that actually substituted, even slight substitution may involve a very material expenditure of iodine, in fact it is possible by continuous shaking and addition of water to divert practically all the "exterior" iodine to the formation of iodoantipyrine. If, on the other hand, titration is carried on in the presence of a strong mineral acid, little or no substitution takes place, but here again

obstacles arise in the form of conditions favoring oxidation, so that even with moderate shaking the hydriodic acid liberated by the mineral acid is subjected to uninterrupted oxidation. Furthermore, since the sodium iodide formed in the course of the titration is continuously converted into hydriodic acid, the cycle becomes practically complete and iodine values are limited only by the willingness of the operator to persist in shaking and titrating. It will be readily appreciated from the above how extremely difficult it is to create and maintain conditions effectively excluding both substitution and oxidation. Nevertheless, it developed that the use of solid potassium or sodium bicarbonate in the alcoholic solution of the periodide, together with a few cubic centimeters of glacial acetic acid, yielded fairly concordant results. Titration also of the periodide in alcoholic solution with standard alcoholic thiosulfate gave equally satisfactory values for the "exterior" or additive iodine. Total iodine was determined by treating the sample either according to Carius or with sulfur dioxide<sup>1</sup> in aqueous-acetic acid solution, followed by precipitation with silver nitrate.

The estimation of antipyrine was effected in form of its iodo derivative by dissolving 0.5 g. of the periodide in about 10 cc. alcohol-free chloroform and shaking vigorously at intervals in a separatory funnel with a mixture of 10 cc. sodium bicarbonate solution, 25 cc. 0.1 *N* iodine and 50 cc. water. After standing a few minutes, excess of iodine is removed by the addition of a crystal of thiosulfate, and the resulting iodoantipyrine isolated by extraction with three 25 cc. portions chloroform, each portion being subsequently washed in a second separatory with 5 cc. water prior to withdrawal through cotton to a 100 cc. beaker, and later evaporated to apparent dryness on the steam bath. The residual iodoantipyrine is thereupon dried one-half hour at 110° in an air bath, then cooled and weighed. The conversion factor for antipyrine is 0.5990. The values resulting from the estimation of this substance as a whole were found to be more reliable than those obtained in determining the elemental constituents carbon and hydrogen, for reasons already pointed out.

Molecular-weight determinations made by the boiling point method, involving absolute alcohol and chemically pure acetone, yielded the values 344 and 346, respectively. These values, while concordant enough in themselves, are unquestionably low and indicate marked dissociation. The molecular weight of the simplest possible formula is, as will presently appear, 442.9. No determinations were attempted by the freezing point method owing to the lack of suitable solvents.

In view of the method of preparation, as also of the fact that antipyrine as such is recoverable from the crystalline periodide, any idea that iodoantipyrine may participate in its formation need not receive serious con-

<sup>1</sup> Cf. Emery and Palkin, *J. Ind. Eng. Chem.*, 7, 519 (1915).



sideration. Accordingly, the choice of a suitable formula must be made solely from those involving antipyrine, hydriodic acid and iodine as component parts of the periodide molecule. Of the many possible combinations, only three perhaps deserve mention, namely:  $C_{11}H_{12}N_2O.HI.I$ ,  $(C_{11}H_{12}N_2O)_2.HI.I_3$  and  $(C_{11}H_{12}N_2O)_3.(HI.I_2)_2$ , the antipyrine and total iodine content of which are approximately the same. Comparison of the analytical findings, however, with the percentage composition of the remaining factors, particularly of "exterior" iodine, tends to confirm the third formula as being the most probable.

	Calc. for $C_{11}H_{12}N_2O.HI.I$	Calc. for $(C_{11}H_{12}N_2O)_2.HI.I_3$	Calc. for $(C_{11}H_{12}N_2O)_3.(HI.I_2)_2$	Found.				
C.....	24.4	24.4	29.8	.....	.....	.....	.....	31.2
H.....	2.9	2.8	2.8	.....	.....	.....	.....	3.1
N.....	6.3	6.3	6.3	.....	.....	.....	.....	6.8
I (total).....	57.3	57.4	57.3	.....	56.8	56.9	57.0	56.8
I ("exterior")..	28.6	42.5	38.2	36.8	38.2	37.8	38.0	37.5
Antipyrine...	42.5	42.5	42.4	.....	.....	42.6	42.9	43.2

**Diantipyrine Hydriodo-diodide,  $(C_{11}H_{12}N_2O)_2.HI.I_2$ .**—This compound was obtained substantially as follows: To a solution of 4.9 g. antipyrine in 25 cc. alcohol (95%) were added 3.37 g. iodine dissolved in 25 cc. alcohol (containing an amount of hydriodic acid equivalent to 4.45 g. potassium iodide and prepared in the manner previously described). The volume of the liquid was further increased by the addition of 50 cc. of alcohol, the whole then warmed on the steam bath to about  $50^\circ$  and thereupon diluted with 25 cc. of water with constant stirring. The solution was allowed to cool very gradually in the open until crystals began to appear, whereupon the cooling was continued in a refrigerator. The resulting product was filtered by suction on a small filter plate, washed several times with 60% alcohol previously saturated with iodine, then dried in the air by spreading over filter paper on a porous plate, and finally by placing in a desiccator for about 24 hours. The periodide appeared in the form of slender glistening ruby-red needles melting at  $96-7^\circ$ . Crystals obtained from the mother liquor were in nearly every instance found to be impure, the product being, as a rule, dull-lustered and lighter in color, and possessing a lower iodine content than the first crop. Recrystallization is inadvisable. On subjecting the crystals to analysis, difficulties developed very similar to those already described for the preceding periodide. By observing the necessary precautions, however, results were obtained satisfactorily confirming the composition as indicated in the caption, namely:  $(C_{11}H_{12}N_2O)_2.HI.I_2$ .

Calc. for  $(C_{11}H_{12}N_2O)_2.HI.I_2$ : 51.0% total I; 33.5% exterior I; 49.6% antipyrine.  
Found: I, 50.9, 50.4, 51.3; I, ext., 32.8, 33.0; antipyrine, 49.7.

**Crystalline Periodides of Iodoantipyrine.**—The isolation of these compounds was effected in two stages, *viz.*: (i) Preparation of iodoanti-

pyrine, and (2) preparation of the periodides themselves. Iodoantipyrene, first reported by Dittmar<sup>1</sup> and prepared by the action of iodine trichloride on antipyrin, may be conveniently made as follows: 2 g. antipyrine and 1 g. sodium bicarbonate were dissolved in 100 cc. of water, the solution heated to 50° and a 0.1 *N* solution of iodine slowly added with constant stirring until a faint yellow coloration persisted. On cooling, colorless needles separated which were filtered by suction and washed several times with a little water. A second crop of crystals may be obtained by concentrating the filtrate on the steam bath and allowing the residual solution to stand for some time in the cold. The crystals as first obtained were recrystallized once from a hot 50% alcoholic solution. When thoroughly dried, the product melted at 160–1°.

Calc. for  $C_{11}H_{11}N_2IO$ : I, 40.4%. Found: I, 40.4, 40.5.

**Di-iodoantipyrene Hydriodo-diiodide**,  $(C_{11}H_{11}N_2IO)_2.HI.I_2$ . — This compound was prepared in the following manner: An alcoholic solution of hydriodic acid (obtained by treating 0.4 g. potassium iodide dissolved in 0.2 cc. water with 0.3 cc. conc. hydrochloric acid and 12 cc. absolute alcohol, and subsequent filtering from potassium chloride) and 0.51 g. iodine was poured into a 100 cc. beaker in which 1.24 g. iodoantipyrene had been previously dissolved in 12 cc. warm alcohol. Water was gradually added with constant stirring to the appearance of a brown amorphous precipitate, which became crystalline in the course of a few minutes. More water was then added until the total volume was about 55 cc. The ruby red needle-like crystals were thereupon filtered by suction, transferred to the original beaker and washed with several portions of water, stirring and decanting each portion as added, again filtered by suction on a perforated plate and finally dried in the air until odorless. The sample was then subjected to analysis, as also a second one obtained by recrystallizing the products from several other experiments, thus: 1.5 g. of the mixed samples were dissolved in 20 cc. warm alcohol, gradually diluted with water to the appearance of an amorphous precipitate, allowed to stand until crystallization set in, then water again very gradually added with constant stirring until the total volume amounted to 35 cc. The resulting ruby-red needles were thereupon filtered, washed and dried as above described. The titration of the iodine of addition by means of aqueous thiosulfate was effected without difficulty in alcoholic solution in the presence of sodium bicarbonate. Total iodine was determined both by the method of Carius and by the sulfur dioxide method.<sup>1</sup> The estimation of iodoantipyrene was made by extraction with chloroform, evaporation of the solvent and subsequent weighing.

<sup>1</sup> *Loc. cit.*

Calc. for  $(C_{11}H_{11}N_2IO)_2.HI.I_2$ : 62.7% total I; 25.1% exterior I; 5.6% N; 62.2% iodoantipyrine.

Found: total I (I) 62.8, 62.5, (II) 62.9; ext. I (I) 25.2, 25.3, (II) 25.5; N, 5.6; iodoantip., 62.2.

This periodide melts at  $124-5^\circ$ , is readily soluble in acetone and chloroform, less so in alcohol and behaves toward other organic solvents very like the periodides of antipyrine itself.

**Di-iodoantipyrine Hydriodo-tetridide**,  $(C_{11}H_{11}N_2IO)_2.HI.I_4$ .—An iodized alcoholic solution of hydriodic acid (prepared in the manner above described for the diiodide, from 0.2 g. potassium iodide, 0.1 cc. water, 0.15 cc. conc. hydrochloric acid, 12 cc. absolute alcohol and 0.41 g. iodine was added to a warm solution of 0.5 g. iodoantipyrine in 5 cc. alcohol. Water was then added with constant stirring to the formation of an amorphous or tarry precipitate, the mixture was allowed to stand 10 minutes, or until the precipitate became crystalline, then more water was cautiously added with stirring until the total volume amounted to about 30 cc., whereupon the product was allowed to stand one-half hour. The resulting crystals were filtered, washed and dried in much the same manner as specified for the preceding compound. The resulting chocolate-colored prisms melted at  $94-5^\circ$  and gave values for additive iodine about 2% below the theory (I). Two recrystallizations carried out in the same manner as indicated above yielded better results (II). The periodide forms chocolate-colored prisms, very soluble in chloroform and acetone, quite so in alcohol, but insoluble in water. It is rather difficult to prepare in a pure condition.

Calc. for  $(C_{11}H_{11}N_2IO)_2.HI.I_4$ : 70.3 total I; 40.2 ext. I.

Found: (II) 69.7; ext. I (I) 37.9, (II) 40.2.

**Di-iodoantipyrine Hydriodo-hexiodide**,  $(C_{11}H_{11}N_2IO)_2.HI.I_6$ .—The alcoholic solution of hydriodic acid and iodine (prepared in the usual way from 0.2 g. potassium iodide, 0.1 cc. water, 0.15 cc. conc. hydrochloric acid and 12 cc. absolute alcohol) was added to 0.415 g. iodoantipyrine dissolved in 25 cc. warm alcohol, the resulting mixture gradually diluted with water until a tarry precipitate formed, set aside until crystallization took place (about 10 minutes), then more water added with constant stirring until the volume totalled 75 cc. The crystals, filtered, washed and dried as in the case of the preceding compound, formed dark green glistening needle-like prisms melting at  $97-8^\circ$ , amounting in weight to 0.81 g. The product was redissolved in 12 cc. alcohol and again brought to crystallization by the gradual addition of 25 cc. water. The resulting crystals, isolated as in the first instance, amounted to 0.57 g. and gave the same melting point as before.

Calc. for  $(C_{11}H_{11}N_2IO)_2.HI.I_6$ : 75.3 total I; 50.2 ext. I; 41.4 iodoantipyrine.

Found: total I, 75.3, 75.0; ext. I, 50.3; iodoantip., 41.4, 41.5.

**Crystalline Periodides of Pyramidone (Dimethylamino-antipyrine).—**In the preparation of these compounds, two essential operations were involved, namely: isolation (1) of the hydriodide of pyramidone, and (2) of the periodide of the latter product.

**Pyramidone Hydriodide,  $C_{13}H_{17}N_3O.HI$ .—**This salt was first reported by Nardelli and Paolini,<sup>1</sup> who employed it medicinally in aqueous solution with pyramidone. Later, Cousin<sup>2</sup> actually isolated the salt and at the same time the periodide,  $C_{13}H_{17}N_3O.HI.I_2$ , the former resulting from operations in aqueous, the latter in aqueous-alcoholic solution. The hydriodide was obtained by us in two ways: 1st. 2 g. pyramidone were dissolved in 10 cc. chloroform, to which was then added an alcoholic solution of hydriodic acid (from 1.66 g. potassium iodide, 1.5 cc. water, 1 cc. conc. hydrochloric acid and 20 cc. alcohol), the resulting liquid further diluted with alcohol to a final volume of about 50 cc. Ethyl ether was then added with constant stirring until the solution became slightly turbid and a white precipitate of the hydriodide began to form. After allowing the precipitate to settle for an hour, more ether was added to the turbidity point and the mixture again allowed to stand. The product was then filtered by suction and washed a few times with ether. For purposes of analysis, recrystallization was resorted to by dissolving in a small quantity of warm alcohol and reprecipitating with ether as above described. The crystalline product was again filtered by suction, washed several times with ether and dried for a day in the air. Thus prepared, pyramidone-hydriodide appeared as a fine white granular powder, darkening at 190° and melting at 196–7° (200° Cousin), and becoming yellow on long standing. 2nd. 5 g. pyramidone were dissolved in 10 cc. ethyl acetate and treated with gaseous hydriodic acid until the liquid ceased to yield a precipitate. The resulting needle-like prisms were filtered by suction, washed several times with ether and dried in the air. The melting point was the same as that observed for the granular preparation.

Calc. for  $C_{13}H_{17}N_3O.HI$ : 35.3% I. Found: 35.4, 35.7.

**Pyramidone Hydriodo-diiodide,  $C_{13}H_{17}N_3O.HI.I_2$ .—**To a solution of 1 g. of the hydriodide in hot glacial acetic acid (30 cc.) were added 0.7 g. iodine dissolved in 10 cc. acetic acid and the mixture allowed to stand one day in a shallow dish. The resulting crystals were filtered by suction, washed a few times with a small quantity of acetic acid (36%) and dried in the air until odorless. The compound had the form of fine ruby red needles, softening at about 180° and melting to a brownish oil at 190°. Titrations of this and the following periodide were carried out in a mixed solution of alcohol and acetic acid.

<sup>1</sup> D. R. P. 180,120 (1905); Friedlaender, *Fortschritte der Teerfarben-Fabrikation*, p. 982 (1905–7).

<sup>2</sup> *J. pharm. chim.*, [6] 28, 158; 29, 49 (1908–9).

Calc. for  $C_{13}H_{17}N_3O.HI.I_2$ : 62.1% total I; 41.4 ext. I. Found: 62.2 total; 41.5 ext.

A periodide of like composition was obtained by Cousin<sup>1</sup> in the form of brown needle-like crystals from an aqueous alcoholic solution of the hydriodide and iodine. He reports also the formation of the same compound by the interaction of pyramidone (1 mol) and iodine (3 mol) in alcoholic solution. No melting point, however, is given.

**Pyramidone Hydriodo-triiodide,  $C_{13}H_{17}N_3O.HI.I_3$ .**—This compound was obtained by dissolving 1.2 g. of the hydriodide in about 50 cc. hot alcohol and treating the solution with 1.6 g. iodine likewise dissolved in warm alcohol (20 cc.). Water was then added to the liquid with constant stirring until a slight turbidity resulted, whereupon the mixture was allowed to stand several hours in the cold. Small, heavy, greenish glistening leaflets somewhat resembling herapathite gradually collected on the bottom of the container. The crystals were filtered by suction, washed several times with 50% alcohol and finally dried in the air until practically odorless. A second crop of crystals was obtained by diluting the filtrate with water and allowing it to stand for several hours. The melting point of this periodide was found to be at  $155-6^\circ$ .

Calc. for  $C_{13}H_{17}N_3O.HI.I_3$ : 51.4% ext. I. Found: 51.4.

It may not be amiss to mention that both periodides of pyramidone herein described can, with equal facility, be prepared directly from the base itself, without first isolating the hydriodide, by dissolving the components in alcohol and allowing the resulting addition product to slowly separate by crystallization.

### Summary.

Conclusions have already been drawn relative to the behavior of antipyrine toward iodized potassium iodide in aqueous solution, and to the nature and composition of the tarry precipitates resulting therefrom. (Cf. p. 2172.)

The hitherto unreported periodides,  $(C_{11}H_{12}N_2O)_3.(HI.I_2)_2$ ,  $(C_{11}H_{12}N_2O)_2.HI.I_2$  and  $(C_{11}H_{11}N_2IO)_2.HI.I_2$ , derivative of antipyrine and iodoantipyrine, respectively, were isolated in crystalline form and characterized from tars obtained by the action of iodized potassium iodide on aqueous acid solutions of antipyrine and iodoantipyrine, respectively.

These same compounds, together with the crystalline periodides,  $(C_{11}H_{11}N_2IO)_2.HI.I_4$  and  $(C_{11}H_{11}N_2IO)_2.HI.I_6$ , were more conveniently prepared and in purer form by dissolving their components in alcohol and allowing the resulting solution to slowly deposit crystals.

Two crystalline periodides of pyramidone,  $C_{13}H_{17}N_3O.HI.I_2$  and  $C_{13}H_{17}N_3O.HI.I_3$ , were prepared and characterized, the latter having never before been described.

WASHINGTON, D. C.

<sup>1</sup> *Loc. cit.*

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN.]

## THE COLORS PRODUCED BY RESORCINOL IN SOLUTIONS OF CERTAIN SALTS AND THE USE OF THESE COLORS AS A MEANS OF DETECTING RESORCINOL IN THE PRESENCE OF OTHER PHENOLS.

By FRANCIS C. KRAUSKOPF AND GEORGE RITTER.

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### Introduction.

It has been found that resorcinol in an ammoniacal solution with zinc salts produces a blue color. This has been used as a colorimetric determination of small quantities of zinc.<sup>1</sup>

In attempting to use this color reaction as a qualitative test for zinc it was found that cobalt, nickel and cadmium also produce characteristic colors. The color produced by cobalt is violet, that by nickel bluish violet, and that by cadmium blue. These colors being similar to that produced by zinc it was found to be impracticable to use this method as a qualitative test for zinc salts.

It was then thought that this color reaction might be used as a means of detecting resorcinol in the presence of other phenols. Since cobalt salts give the most intense coloration, these seemed the most suitable for the purpose.

Accordingly this study is divided into two parts: First, a determination of the conditions under which ammoniacal solutions of these salts and resorcinol will with regularity produce these characteristic colors, and the determination of whether or not other phenols will develop similar colors. Second, the use of these color reactions for the detection of resorcinol in the presence of other phenols.

Pieroni and Girardi<sup>2</sup> found that when a solution of pyrogallol in pyridine, mixed with a pyridine solution of a nickel salt, is diluted with water, various colors are produced, dependent on the relative amounts of nickel, pyrogallol, water and pyridine used. It was also found that salts of silver and mercury, when used in the place of the nickel salts, produced colors of a similar nature.

The authors considered these colors to be caused by the reduction, by means of the pyrogallol, of the salts to the metal in the colloidal state.

It seemed reasonable to suppose that the colors produced by the resorcinol were also due to the reduction of the salt to the metal in the colloidal state. This was confirmed by the fact that the color would not dialyze through parchment, and that the colloidal nature could be easily seen by means of the ultramicroscope.

<sup>1</sup> Cerdan and De la Puente, *Anales Soc. espan. fis. quim.*, 2, 98-108 (1913).

<sup>2</sup> *Kolloid Zeit.*, 15, 159 (1914).

### Part I. Experimental.

In order to determine the best conditions under which these characteristic colors develop, an attempt was made to answer the following questions:

Does the depth or shade of the color developed depend upon the salt of cobalt used?

Does the depth of color vary after a certain concentration of cobalt is reached?

Does the depth of color vary after a certain concentration of resorcinol is reached?

What concentration of ammonia is most favorable for the color development?

Knowing that an access of air influences the reaction, will the color develop most uniformly with total, partial, or non-exclusion of air?

What colors, if any, are produced by some of the other phenols?

**Solutions Used.**—(1) One per cent. solution of each of the following: resorcinol, pyrocatechin, hydroquinone, carbolic acid, pyrogallie acid.

(2) Solutions of cobalt chloride, cobalt nitrate, and cobalt sulfate, each containing 0.0004 g. of cobalt per cc.

(3) Ammonium hydroxide 0.90 sp. gr.

Test solutions as indicated below were prepared in Nessler tubes. These tubes were all of the same size and shape in order to make a fair comparison of the depth and shade of color. These tubes were immediately closed with rubber stoppers and inverted twice to thoroughly mix the liquids. They were then placed in a rack and allowed to stand until the color reaction became pronounced.

**Experiment I.**—Solutions were made up as follows:

Ammonium hydroxide, 4 cc., resorcinol solution, 1 cc., solution of cobalt sulfate, cobalt chloride, or cobalt nitrate, 1 cc., water to make 50 cc. Allowed to stand 3 hours.

The violet color obtained in all cases was of the same depth and shade, which shows that the various salts of cobalt used have the same effect on the reaction.

**Experiment II.**—Each solution contained:

Ammonium hydroxide, 4 cc., resorcinol 1 cc., varying amounts of cobalt chloride, water to make 50 cc. Allowed to stand 3 hours.

0.5 cc. of cobalt chloride produced a faint violet color; any amount between 1 cc. and 5 cc. produced the same shade and depth of violet color, which shows that nothing is to be gained by using more than 1 cc. of cobalt chloride solution.

**Experiment III.**—Each solution contained:

Resorcinol, 1 cc., cobalt chloride, 1 cc., varying amounts of ammonium

hydroxide, water to make 50 cc. Allowed to stand 3 hours. Results are seen in Table I.

TABLE I.

NH <sub>4</sub> OH, 1 cc.	2 cc.	3 cc.	4 cc.	5 cc.
Color . . . brown ppt.	slight violet and brown ppt.	violet and brown ppt.	violet	violet

This shows that if less than 4 cc. of ammonium hydroxide is used with 1 cc. of cobalt chloride, cobalt hydroxide is precipitated and the color is to some extent indistinct. If more than 4 cc. is used the color is not deepened.

**Experiment IV.**—Solutions contained:

Ammonium hydroxide, 4 cc., cobalt chloride, 1 cc., varying amounts of resorcinol, water to 50 cc. Allowed to stand 3 hours. These results are found in Table II.

TABLE II.

Resorcinol, cc. . . . .	0.3	0.5	1	2
Color . . . . .	faint violet	violet	deep violet	deep violet

This establishes the fact that 1 cc. of resorcinol gives the same results as a larger amount, but less than 1 cc. has a tendency to make the color thin and indistinct.

**Experiment V.**—Solutions contained:

Ammonium hydroxide, 4 cc., cobalt chloride, 1 cc., resorcinol, 1 cc., water to 100 cc. or to 115 cc.

In the case where the solution was made up to 100 cc., but 15 cc. of air was left above the solution. Where the solution was made up to 115 cc., air was completely excluded from the tube. This was accomplished by fitting a one-hole rubber stopper with a short glass tube drawn to a capillary at one end. By using this stopper some of the liquid was forced out through the capillary tube, thus excluding all air from the liquid. The tube was then sealed by placing the point of the capillary in a Bunsen flame. In order to obtain the same depth of color as in the solutions used before this, it was necessary to allow the tubes containing 100 cc. of solution and 15 cc. of air to stand five hours instead of three. In the tubes from which the air was completely excluded the colors produced were the most satisfactory as far as the shade was concerned. They were exact duplicates of one another in a given time, but the time required was increased from three hours, in the presence of air, to ten when air was excluded.

In cases where air was in contact with the solutions the beautiful violet color would change to a dull green and finally to a brownish black. An ammoniacal solution of resorcinol turns brown when in contact with air, so that this change to green and then to brown was no doubt caused by this color change of the resorcinol itself. However, when the solution was stoppered so as to exclude all air the violet color develops much more



slowly, but after reaching a certain intensity retains the same color and depth of color for an indefinite time.

**Experiment VI.**—Solutions contained:

4 cc. of ammonium hydroxide, 1 cc. of cobalt chloride, 1 cc. of either carboic acid, pyrocatechin, hydroquinone, or pyrogallic acid and water to 50 cc. Allowed to stand three hours.

The color produced by pyrocatechin, hydroquinone, or pyrogallic acid was brown. Carboic acid produced no color.

**Part II. Experimental.**

Having thus become familiar with the characteristic colors of cobalt and resorcinol when solutions of the two are mixed, and with the conditions under which these color reactions best take place, it was thought that these reactions might be used as a means of detecting resorcinol in the presence of other phenols.

Test solutions similar to those shown in Experiments I to VI were prepared in Nessler tubes. At the beginning of each series of experiments a blank sample containing no resorcinol was run. This formed a basis for color comparison with samples containing resorcinol.

The samples in all cases were treated under the same conditions, and allowed to stand the same length of time before the reading was taken. After the sample was prepared, the Nessler tube was immediately closed with a rubber stopper, inverted twice to mix liquids, and then placed into a rack until the color developed. The amounts of each compound per sample and the results are shown in Tables III to V inclusive.

TABLE III.

H <sub>2</sub> O. Cc.	Res. Cc.	Pyrocatechin. Cc.	Color.	H <sub>2</sub> O. Cc.	Res. Cc.	Pyrocatechin. Cc.	Color.
50	..	1	brown	100	..	1	brown
50	1	1	cherry	100	1	1	cherry
50	1	2	reddish brown	100	1	2	brown
50	1	3	brown	100	1	2	brown

TABLE IV.

H <sub>2</sub> O. Cc.	Res. Cc.	Hydroquinone. Cc.	Color.
50	..	1	brown
50	1	1	brown
100	1	1	brown

TABLE V.

H <sub>2</sub> O. Cc.	Res. Cc.	Pyrogallic acid. Cc.	Color.
50	..	1	brown
50	1	1	brown
100	1	1	brown

Each test solution in Tables III, IV and V contained in addition 1 cc. of cobalt chloride and 4 cc. of ammonium hydroxide.

These tables show that the presence of hydroquinone, pyrocatechin or pyrogallic acid either prevents the development of the violet color produced by resorcinol alone, or the violet color is completely obscured by the brown color which is produced by the hydroquinone, pyrocatechin, or pyrogallic acid. Since the brown color caused by these phenols appears

only when air is in contact with the solution, several solutions similar to the above were prepared with the tubes completely sealed from the air. In these neither the violet color of the resorcinol nor the brown color of the other phenols appeared even on long standing.

With carbohc acid and resorcinol present the solutions developed no color, even when in contact with air. This would indicate that the presence of the other phenols had an inhibiting effect upon the development of the violet color of resorcinol.

It is also shown that in the presence of these other phenols, resorcinol cannot be detected by this method.

Having found that resorcinol cannot be detected by the method indicated in Tables III to V, an attempt was made to produce colors by which it might be done. It was discovered that by decreasing the amount of ammonium hydroxide and adding a few cubic centimeters of alcohol to a test sample containing resorcinol, allowing it to stand about three minutes, and then shaking, a dark green color is produced.

The reaction of carbohc acid treated in this manner gives a colorless solution. Pyrocatechin, hydroquinone, and pyrogallie acid, when present in considerable amounts, develop a brown color.

Solutions similar to those shown in Tables III to V were prepared in Nessler tubes, only that the amount of ammonium hydroxide was decreased and a few cubic centimeters of alcohol were added. The tubes containing these test solutions were immediately closed with a rubber stopper, and after being allowed to stand from three to five minutes, were vigorously shaken.

The portion of each ingredient per sample and the results are shown in Tables VI to IX.

TABLE VI.

Res. Cc.	Pyrocatechin. Cc.	Color.	Res. Cc.	Pyrocatechin. Cc.	Color.
..	1	brown	1	10	dark green
1	1	dark green	1	20	dark green
1	4	dark green	0.5	20	brownish green

Table VI shows that in 50 cc. of solution, 0.005 g. of resorcinol can be detected in the presence of 0.220 g. of pyrocatechin.

TABLE VII.

Hydro- qui- none. Cc.	Color.
.. 1	brown
1 1	dark green
1 10	green
1 20	brownish green

TABLE VIII.

Car- bolic acid. Cc.	Color.
.. 1	colorless
1 1	greenish yellow
1 10	greenish yellow
1 20	greenish yellow
1 30	yellow tinge

TABLE IX.

Pyro- gallie acid. Cc.	Color.
.. 1	brown
1 1	cherry
1 8	cherry
1 20	slightly cherry

Besides the contents shown in the tables, each test solution contained

1 cc. cobalt chloride, 0.3 cc. ammonium hydroxide,<sup>1</sup> 3 cc. of 95% alcohol, and water to make 50 cc.

Table VII shows that in 50 cc. of solution, 0.010 g. of resorcinol can be detected in the presence of 0.200 g. of hydroquinone.

Table VIII shows that in 50 cc. of solution, 0.005 g. of resorcinol can be detected in the presence of 0.300 g. of carboic acid.

Table IX shows that in 50 cc. of solution, 0.010 g. of resorcinol can be detected in presence of 0.200 g. of pyrogalllic acid.

#### Summary.

(1) Resorcinol in an ammoniacal solution of cobalt salts produces a color distinct from that produced by the other phenols tried.

(2) The best conditons for uniformity of this color development have been determined.

(3) The exclusion of the air from the test solution increases the length of time required for color development.

(4) The presence of certain other phenols either inhibit the formation of the resorcinol color, or else obscure it by the colors they themselves produce. Consequently, resorcinol cannot with certainty be detected with an ammoniacal solution of cobalt by the method indicated in Tables III to V, if these other phenols are present.

(5) Resorcinol as low as 0.001 g. per 50 cc. sample, if shaken with a weak ammoniacal solution of a cobalt salt and a few cubic centimeters of alcohol, develops a dark green color. Pyrocatechin, hydroquinone, and pyrogalllic acid under same conditions develop a brown color, carboic acid produces a colorless solution.

(6) The presence of the other phenols tried does not prevent the formation of the dark green color developed by resorcinol. Thus small amounts of resorcinol can be detected in the presence of comparatively large amounts of certain other phenols.

MADISON, WIS.

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[CONTRIBUTION FROM THE CARBOHYDRATE LABORATORY, BUREAU OF CHEMISTRY,  
UNITED STATES DEPARTMENT OF AGRICULTURE.]

### PREPARATION OF BROMOACETYLGLUCOSE AND CERTAIN OTHER BROMOACETYL SUGARS.

By J. K. DALE.

Received August 19, 1916.

In a recent article<sup>2</sup> E. Fischer published a method for the preparation of bromoacetylglucose which consisted essentially in the action of a saturated solution of hydrobromic acid gas in glacial acetic acid upon glucose pentacetate. Since bromoacetylglucose is an important compound, serving as the basis for the synthesis of many derivatives of glucose, it does not

<sup>1</sup> In Table IX the amount of ammonium hydroxide was 2 cc. for each test solution.

<sup>2</sup> *Ber.*, 49, 584 (1916).

seem out of place to describe a method I have used for its preparation which is somewhat simpler than that given by Fischer.

A saturated solution of hydrobromic acid gas in acetic anhydride was found to react directly with several of the sugars and from the reaction mixture could be isolated the bromoacetyl derivative. By this reaction bromoacetylxylose,<sup>1</sup> bromoacetylcellulose and bromoacetylactose, as well as bromoacetylglucose, were prepared in the crystalline condition with yields of respectively 26, 60 and 77% of the theoretical. Bromoacetylmaltose was also obtained by this method, though only in the amorphous condition. A detailed description of the preparation of bromoacetylglucose is given below; it is typical of the method of preparation of each of the above named compounds.

Twenty-five grams of finely powdered glucose were treated in a large Erlenmeyer flask at room temperature with 125 cc. of acetic anhydride saturated with hydrobromic acid gas. A very vigorous reaction followed, leaving a clear, straw-colored sirup. This was cooled, mixed with 300 cc. of chloroform and the solution washed twice with water, once with enough sodium bicarbonate solution to neutralize the dissolved acids, and then once more with water. After drying with calcium chloride, the chloroform solution was evaporated at 50° under diminished pressure to a thick sirup which was washed into a beaker with a little dry ether. Fifteen to twenty volumes of petroleum ether were added, causing the bromoacetylglucose to precipitate as a thick sirup, which on cooling in an ice bath and being stirred vigorously, solidified in a few minutes to a crystalline mass. It was filtered off on a Büchner funnel and recrystallized by dissolving in 75 cc. of dry ether and evaporating the solution in a current of dry air until it crystallized. The yield of the once recrystallized substance was between 50% and 60% of the theory. Fischer obtained by his method 56% of the theoretical amount.

When bromoacetylglucose was sufficiently pure no trouble was experienced in preserving it in good condition for weeks at a time, but usually more than one recrystallization was necessary for this purpose.

WASHINGTON, D. C.

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[FROM THE INSTITUTE OF THE MEDICAL CHEMISTRY OF KYOTO IMPERIAL UNIVERSITY,  
JAPAN.]

### QUANTITATIVE DETERMINATION OF HIPPURIC ACID IN URINE, BLOOD, MUSCLES AND LIVER: A METHOD.

By Dr. Hiizu Ito.

Received July 28, 1916.

Since Bunge and Schmiedeberg<sup>2</sup> published a well-known method for quantitative determination of hippuric acid in urine in 1876, various

<sup>1</sup> THIS JOURNAL, 37, 2745 (1915).

<sup>2</sup> Bunge u. Schmiedeberg, *Arch. exp. Path. Pharm.*, 6, 233 (1876).

investigators have suggested several methods. These methods may be conveniently classified in three ways: Hippuric acid is determined as such;<sup>1</sup> as nitrogen in glycocholl;<sup>2</sup> as benzoic acid.<sup>3</sup> The method here described follows the third scheme. It is generally acknowledged that, in extracting the experimental material, an extracting apparatus with boiling ether gives a better result than a separatory funnel. For this reason an extracting apparatus, designed as illustrated in Fig. 1 was used. The main tube *a* has two branch-tubes *b* and *c*, one of which, *b*, serves for the ascending petroleum-ether vapor, and the other, *c*, for the returning petroleum ether which, collecting at the lower small opening *d* of the branch tube *c* closes the latter, and prevents the ascent of vapor except through the other branch tube *b*. The flask *f* with petroleum ether is connected with the apparatus, and is immersed in an electric water bath, kept at 80–90°, which keeps the solution boiling. This apparatus is also adapted for extraction with ethyl ether.

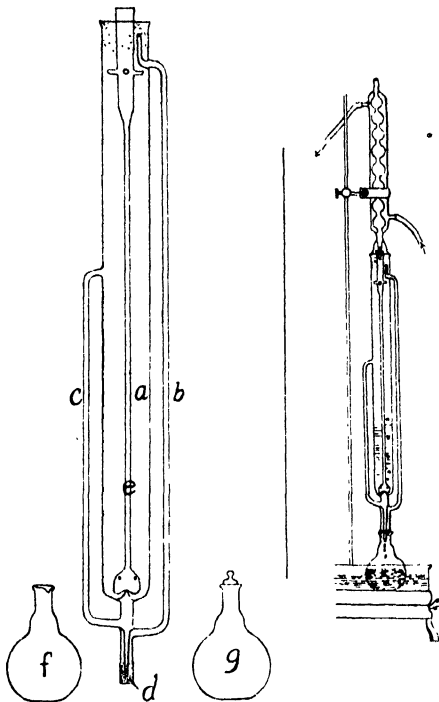


Fig. 1.

TABLE I.

Hippuric acid 0.0328 g., equal to 0.0224 g. benzoic acid.				Hippuric acid 0.4264 g., equal to 0.2906 g. benzoic acid.			
Time for hydrolyses.	Conc. of NaOH.	Benzoic acid recov- ered (g.).	Benzoic acid ac- counted for.	Time for hydrolyses.	Conc. of NaOH.	Benzoic acid recov- ered (g.).	Benzoic acid ac- counted for.
8 hours	20%	0.0190	84.8%	8 hours	20%	0.2833	97.5%
8 hours	25%	0.0210	93.8%	8 hours	25%	0.2872	98.8%
12 hours	20%	0.0202	90.2%	12 hours	20%	0.2829	97.4%
12 hours	25%	0.0222	99.1%	12 hours	20%	0.2829	99.0%
16 hours	20%	0.0219	97.8%				

In order to determine the best conditions for hydrolysis of the hippuric

<sup>1</sup> *Loc. cit.*

<sup>2</sup> Henriques u. Soerensen, *Z. physiol. Chem.*, 63, 27 (1909); 64, 120 (1910); Blumenthal, *Z. klin. Med.*, 40, 339 (1900).

<sup>3</sup> Jaarveld u. Stockvis, *Arch. exp. Path. Pharm.*, 10 (1879), 268; Folin, *J. Biol. Chem.*, 11, 257 (1912); Steenbeck, *Ibid.*, 11, 201 (1912).

acid varying concentrations of NaOH were tried. The results obtained after extracting the benzoic acid with petroleum ether are given in Table I.

It was thus found that the maximum result could be obtained by using 25% NaOH and 12 hours' boiling for the hydrolysis, and the following experiments were, therefore, carried out under these conditions. The results of determinations of hippuric acid in urine, blood, muscles and liver are shown in Tables II, III, IV and V.

To establish the purity of the recovered benzoic acid, its melting point was determined and found to be  $116.0-120.0^{\circ}$  ("uncorrected"). Furthermore, microscopical examination of the crystal form of the substance proved its identity with benzoic acid.

Procedures for the quantitative determination of hippuric acid in urine and in other mixtures will be described in detail in the following:

### Experimental.

**1. Urine.**—A quantity of fresh rabbits urine was divided into two equal portions; to the one portion a fixed quantity of hippuric and benzoic acids was added and the other was used as a control. Each portion was made faintly alkaline with sodium carbonate, and evaporated nearly to dryness and the residue was thoroughly extracted with absolute alcohol. After evaporating off the alcohol the residue was dissolved in water. The solution was transferred to the apparatus described above and was extracted for 12 hours with pure dry ethyl ether (in this case the solution must be alkaline), which dissolved the resin substance, while the sodium hippurate and sodium benzoate remained undissolved. The solution

was then transferred to a porcelain evaporating dish, a little animal charcoal was added and the ethyl ether was driven off completely. The solution, after having been poured into the apparatus, was made slightly acid with hydrochloric acid, and extracted with petroleum ether b. p.  $30-60^{\circ}$  for 48 hours. In this case the benzoic acid alone dissolved, while the hippuric acid remained undissolved. After cooling, the petroleum ether in the flask *f* was filtered into the weighed flask *g* and the petroleum ether was evaporated by a stream of dry air. The benzoic acid crystallized beautifully on the inner wall of the flask *g*.

The solution, which contained hippuric acid only, was neutralized

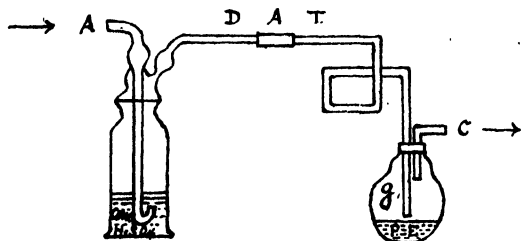


Fig. 2.—Evaporating apparatus. Petroleum ether in the flask (*g*); A = Air, D. A. T. = dry air tubing, P. E. = petroleum ether, and C = connection with a suction tube. Arrows show direction of air current.

cooling, the petroleum ether in the flask *f* was filtered into the weighed flask *g* and the petroleum ether was evaporated by a stream of dry air. The benzoic acid crystallized beautifully on the inner wall of the flask *g*.

with sodium carbonate, and 15 cc. of 50% NaOH were added to it. The mixture was then carefully concentrated to 30 cc., and was boiled in a 200 cc. Kjeldahl flask with an upright condenser for 12 hours. It was then transferred completely to a porcelain evaporating dish concentrated to as small a volume as possible, after adding a little animal charcoal. After it was cooled, 30% hydrochloric acid was carefully added drop by drop with continuous stirring. The acidified solution was now transferred to the extracting apparatus, and extracted with petroleum ether for 72 hours. The petroleum ether was filtered off in the flask mentioned above and evaporated as already described. The hippuric acid was weighed as crystalline benzoic acid. The results are given in Table II.

TABLE II.

Benzoic acid added (80 cc. urine).					Hippuric acid added (80 cc. urine).				
Gram benzoic acid added as sodium benzoate.	Gram benzoic acid recovered.	Benzoic acid in control urine.	Difference.	Percentage of benzoic acid accounted for.	Gram benzoic acid calc. from hippuric acid added.	Gram benzoic acid recovered.	Gram benzoic acid in control urine.	Difference.	Percentage of benzoic acid accounted for.
0.2768	0.2770	0.0039	0.2731	98.7	0.2677	0.2691	0.0090	0.2601	97.2
0.2054	0.2075	0.0045	0.2030	98.8	0.1747	0.1742	0.0077	0.1665	95.3
0.1961	0.2024	0.0067	0.1957	99.8	0.1938	0.2018	0.0136	0.1882	97.1
0.1124	0.1138	0.0030	0.1108	98.6	0.0812	0.0848	0.0064	0.0784	96.6
0.0631	0.0652	0.0042	0.0610	96.7	0.0460	0.0512	0.0081	0.0431	93.7

2. **Blood.**—The defibrinated blood of a cow or a rabbit was divided into two equal portions; to one a fixed quantity of hippuric acid was added and the other was used as a control. Each portion was diluted five times with water, neutralized with weak hydrochloric acid, and heated on a water bath. In this treatment, protein coagulated completely with the fats, and deposited at the bottom of the beaker with a clear layer on its top. After 24 hours' standing, it was filtered through by suction, and repeatedly washed with hot water. The residue together with the filter paper was ground in a glass mortar, adding water, and again filtered with suction. This treatment was repeated several times. The filtrate was then made faintly alkaline, evaporated nearly to dryness, and the residue was thoroughly extracted with absolute alcohol. In the case of blood, it was not necessary to remove the benzoic acid, for none was added to it and normal blood does not contain benzoic acid. The subsequent treatment was the same as in urine. The results are tabulated as follows:

TABLE III.

Cc. of blood.	Gram hippuric acid added.	Gram benzoic acid calc. from hippuric acid.	Hippuric acid as benzoic acid recovered.	Hippuric acid, as benzoic acid in control blood.	Difference.	Percentage of benzoic acid accounted for.
40 (blood of cow).....	0.3943	0.2687	0.2508	0.0042	0.2466	91.8
50 (blood of cow).....	0.3245	0.2211	0.2064	0.0032	0.2032	91.9
40 (blood of rabbit)...	0.2840	0.1935	0.1735	0.0024	0.1734	89.6

**3. Muscle.**—Muscles, which were finely cut, were divided into two equal portions. Each portion was ground in a glass mortar with addition of some water and was then heated. A fixed quantity of hippuric acid was added to the one portion and stirred well, the other was the control. Each portion was filtered through muslin, having been washed with hot water repeatedly, and was pressed dry. The residue was again ground in glass mortar and filtered through muslin as before and this treatment was repeated several times. The filtrate was made neutral or weakly acid, and evaporated. The protein in the filtrate coagulated with the fats upon heating on a water bath and the whole was filtered by suction, and was washed with water several times. The filtrate was evaporated nearly to dryness and the residue was thoroughly extracted with absolute alcohol. After this treatment, the procedure was the same as in the case of blood. The results are given in Table IV.

TABLE IV

Grams of muscles.	Gram hippuric acid added.	Benzoic acid calc. from hippuric acid.	Hippuric acid, as benzoic acid recovered.	Hippuric acid, as benzoic acid in the control.	Difference.	Percentage of benzoic acid accounted for.
50	0.3572	0.2434	0.2243	0.0008	0.2235	91.8
70	0.3348	0.2282	0.2077	0.0016	0.2061	90.3
100	0.2197	0.1497	0.1326	0.0011	0.1315	87.8

**4. Liver.**—The same treatment as in the case of muscles was applied. The results are given in Table V.

TABLE V.

Grams of liver.	Gram hippuric acid added.	Benzoic acid, calc. from hippuric acid.	Hippuric acid, as benzoic acid recovered.	Hippuric acid, as benzoic acid in the control.	Difference.	Percentage of benzoic acid accounted for.
50	0.4132	0.2816	0.2628	0.0016	0.2612	92.8
50	0.3750	0.2556	0.2331	0.0010	0.2321	90.8
50	0.2581	0.1759	0.1566	0.0012	0.1554	88.3

For the determination of hippuric acid the investigators mentioned in the foot-note of p. 2189, took great pains to obtain the purest possible hippuric acid and at the same time to secure the largest quantitative yield. The effort here described has been to simplify the method by means of a suitable extraction apparatus and to obtain the most satisfactory results in both of these respects.

### Summary.

(1) The method proposed can be well applied to the quantitative determination of hippuric acid in urine and similar materials.

(2) The method has the advantage of simplicity of treatment and of giving fairly accurate results.



[CONTRIBUTION FROM THE DIVISION OF AGRICULTURAL BIO-CHEMISTRY OF THE UNIVERSITY OF MINNESOTA.]

## MODIFICATION OF THE PRATT METHOD FOR THE DETERMINATION OF CITRIC ACID.

By J. J. WILLAMAN.

Received August 11, 1916.

In working with Pratt's method<sup>1</sup> for the determination of citric acid, considerable difficulty was encountered in getting duplicate determinations to agree. This difficulty was mentioned in the 1912 report of the Association of Official Agricultural Chemists,<sup>2</sup> but no suggestions were made for remedying it. It is believed that the modifications described herein will give very satisfactory results.

### Discussion of Process.

The primary operations in this method are the fractional oxidation of the citric acid to acetone by means of potassium permanganate, the removal of the acetone as fast as formed by distillation, the formation of an insoluble mercury-acetone complex by boiling with mercuric sulfate, and the weighing of this precipitate. A thorough study has been made of each step of the process, in the attempt to discover all the influencing factors and the combination of procedures that would give the most satisfactory results. A discussion of the various investigations follows:

**1. Fractional Oxidation.**—The process is purely empirical, the results varying with each change of conditions. The potassium permanganate attacks any organic substance that may be present along with the citric acid, distributing itself among them according to the ease with which each is oxidized. Among the substances likely to be present in working with plant products are other acids brought down by the barium acetate, and sugars and coloring matter occluded by the barium precipitate. These cannot be washed out completely, hence are always present in greater or less amount and capable of consuming permanganate. Acetone itself, the desired end-product of the oxidation of the citric acid, can of course be further oxidized; hence the necessity of removing it as fast as formed. It was found that the more dilute the solution of citric acid is, the less the acetone obtained. This is undoubtedly due to the fact that if only a small amount of citric acid is present at the point of contact between the drop of permanganate and the boiling liquid, the oxidation will proceed beyond the acetone stage before the acetone can escape and before the drop of permanganate is consumed. Several factors, then, would tend to give larger yields of acetone; *viz.*, (1) more

<sup>1</sup> David S. Pratt, "Determination of Citric Acid," U. S. D. A., Bur. of Chem., *Circ. 88* (1912).

<sup>2</sup> "Proceedings of the Twenty-Ninth Annual Convention of the Association of Official Agricultural Chemists," 1912; U. S. D. A., Bur. of Chem., *Bull. 162*, 60-62.

concentrated solution of citric acid, (2) less concentrated solution of permanganate, (3) the presence of substances other than citric acid to partially consume the permanganate, (4) rapid boiling and slow addition of permanganate.

In Table I are presented the results of a few of the experiments which were made to determine the effect of various changes of conditions on the yield of acetone. The several groups of determinations illustrate the four points enumerated above.

TABLE I.

Effect of Various Changes of Conditions of Oxidation on the Yield of Acetone.

Factor under observation.	Citric acid present. Mg.	Vol. of soln. start. Cc.	Strength of $\text{KMnO}_4$ soln., g. per liter.	Added subs. other than citric acid.	Citric acid recovered.	
					Mg.	%.
Vol. of soln. of citric acid at start.....	25	400	0.50	.....	17.7	70.8
	25	200	0.50	.....	18.9	76.0
	25	100	0.50	.....	21.9	87.6
Conc. of citric acid.....	25	400	0.35	.....	18.6	74.4
	50	400	0.35	.....	85.3	85.3
	150	400	0.35	.....	133.7	89.1
	50	100	0.20	.....	46.9	93.8
Strength of $\text{KMnO}_4$ soln.....	50	100	0.50	.....	45.2	90.4
	50	400	0.35	.....	43.8	87.6
	50	400	0.70	.....	42.0	84.0
Rate of oxidn. of citric acid						
(11 min.).....	50	400	0.70	.....	42.0	84.0
(16 min.).....	50	400	0.70	.....	44.6	89.2
Presence of substances other than citric acid.....				50 mg. tartaric acid <sup>1</sup>	45.4	90.8
	75	100	0.50	50 mg. tartaric acid	75.2	100.2
	50	100	0.20	10 mg. sucrose	48.9	97.8

It is evident that if constant results are to be obtained, a certain set of conditions must be adopted and then rigidly adhered to. This has been done in the proposed modified procedure. A volume of citric acid solution of 100 cc. at the beginning of the operation was chosen as the most convenient; ordinarily with 100 mg. citric acid present and no other oxidizable material, and the permanganate solution of 0.5 g. per liter dropping in at the rate of 120 to 150 drops per minute, the reaction will be complete with a residual volume of 15 to 25 cc. in the flask. Thus the rate of distillation must be a little faster than the rate of flow of the permanganate. The volume of solution and a slightly increased rate of permanganate flow are the only items changed from Pratt's original specifications. Although the presence of substances other than citric acid does tend toward slightly higher results, the effect has been found to be inconsiderable.

<sup>1</sup> Blank determinations were made with these substances, and no mercury precipitate was obtained.

2. **The concentration of Denigès' Solution**, in which the acetone distillate is boiled, has a very marked influence on the amount of mercury-acetone precipitate obtained; the stronger the solution the less the precipitate obtained. This is shown by the data in Table II and may be due either to increased solubility of the compound, or a change in its composition. Whatever the cause, it can be avoided by always having the same concentration of mercuric sulfate. Pratt's directions call for 30 to 40 cc. of Denigès' solution in the distillate, but do not specify the volume of that distillate. Since the smaller the amount of oxidizable material, the less is the time required for the operation, the smaller is the distillate, and the more concentrated is the mercuric sulfate. The writer has adopted, therefore, a concentration of 15 cc. of Denigès' solution for each 100 cc. of distillate. The reaction is then proportional with all amounts of citric acid, at least those from 25 to 150 mg. Great accuracy in measuring the distillate is not required; a 700 or 800 cc. Erlenmeyer marked at 300 cc., 400 cc., and 500 cc. does very well.

TABLE II.

The Effect of the Concentration of Denigès' Solution on the Yield of the Acetone-Mercury Compound. 50 Mg. Citric Acid Taken.

Vol. of distillate containing 40 cc.

Denigès' soln., cc.....	200	250	300	350	400	500
Recovery of citric acid, %.....	96.4	96.8	99.3	102.0	100.3	100.7

3. **Amount of the Mercury-Acetone Precipitate Formed.**—This was determined by Pratt by weighing on a Gooch. This has been found less easy and trustworthy than the process of determining the mercury in the precipitate by titration. As the precipitate has a tendency to adhere to the sides of the Erlenmeyer flask in which it is formed, it is difficult to remove it completely to a Gooch. It is, however, readily dissolved by hot 5% hydrochloric acid. The resultant mercuric chloride may be titrated against standard potassium iodide solution according to Personne's method.<sup>1</sup> This procedure was used in all the present experiments, and proved to be rapid and accurate.

4. **The flow of Permanganate** into the oxidation flask in the writer's apparatus, is controlled by a screw pinch-cock on a piece of soft rubber tubing, which replaces the glass dropping funnel in Pratt's apparatus. One end of the rubber tubing is connected to a bent glass tube passing through the stopper of the oxidation flask and ending in a fine nozzle; the other end of the tubing connects with a two liter supply reservoir of permanganate. This arrangement gives better control of the flow of permanganate than the glass-stoppered dropping funnel.

5. **Oxidation Flask.**—A 200 cc. Kjeldahl flask with all but three centimeters of the neck removed is very satisfactory. A 200 cc. side-arm distilling flask is equally good.

<sup>1</sup> *Compt. rend.*, 56, 63; also Sutton's "Volumetric Analysis," 10th edition, 1911, 264.

6. **Removing the Citric Acid** from a plant juice with barium acetate. The writer has adopted a medium of 30% alcohol instead of 50%. It throws out all the citric acid, and only a little of the other acids, as pointed out by Jörgensen.<sup>1</sup> The precipitate is also more granular in this case, and thus more easily filtered and washed.

7. **Quantitative Relation.**—In order to determine the quantitative relation between the citric acid and the potassium iodide used to titrate the mercury of the final product, a series of analyses was made with varying amounts of pure citric acid, using the exact procedure as given below. The potassium iodide solution used, contained 26.70 g. KI per liter. The results are given in Table III. In order to compare the accuracy of these figures with those obtained by Pratt in ascertaining the factor to be used with his gravimetric method, an excerpt is given of his table (the last column was computed by the writer).

TABLE III.

Showing the Determination of the Factor for Potassium Iodide, in Comparison with the Factor in Pratt's Gravimetric Method.

Present method.				Pratt's method.			
Gram citric acid.	KI soln. Cc.	KI soln. per 1 g. citric acid. Cc.	Recovery using value of 0.001906. Per cent.	Gram of citric acid used.	Wt. of precipitate.	Calc. factor.	Recovery using factor 0.220. Per cent.
0.025	12.90	516	98.3	0.020	0.104	0.187	114.4
0.025	12.90	516	98.3	0.049	0.234	0.208	105.1
0.025	13.05	522	99.5	0.052	0.227	0.224	96.0
0.050	26.40	528	100.6	0.080	0.343	0.231	94.3
0.050	26.90	538	102.5	0.097	0.453	0.214	102.7
0.100	52.80	528	100.6	0.104	0.430	0.240	91.0
0.100	52.00	520	99.1	0.104	0.451	0.229	95.4
0.150	78.80	525	100.8	0.104	0.445	0.232	94.1
0.150	79.40	529	100.9	0.104	0.442	0.234	93.5
				0.107	0.510	0.210	104.9
				0.128	0.559	0.229	96.1
				0.128	0.556	0.230	95.6
				0.146	0.679	0.215	102.3
				0.246	1.181	0.208	105.6
				0.491	2.364	0.208	106.0
Average, 524.7 or 1 cc. $\equiv$ 0.001906				Average, 0.220			

According to this procedure, then, 1.0 cc. of a solution of potassium iodide containing 26.70 g. of the salt per liter is equivalent to 1.906 mg. citric acid. For convenience, a solution of potassium iodide of 28.0218 has been adopted, 1 cc. of which is equivalent to 2.0 mg. citric acid.

<sup>1</sup> Jörgensen, "Über die Bestimmung einiger der in den Pflanzen vorkommenden Säuren," *Z. Nahr. Genussm.*, 13, 241 (1907).

### The Modified Method in Detail.

The following solutions are required:

1. Hydrochloric acid, 5% (approximately).
2. Sodium hydroxide, 10%.
3. Phosphoric acid, 6%.
4. Denigès' solution, made as follows: Add about 500 cc. of water to 50 g. of mercuric oxide; then add 200 cc. of concentrated sulfuric acid with constant stirring; make up to a liter, heat on steam bath an hour or two, and filter till clear.
5. Potassium iodide; contains 28.0218 g. pure KI per liter. One cc. of this is equivalent to 2 mg. citric acid under the conditions of the experiment.
6. Mercuric chloride; contains 10.8038 g.  $\text{HgCl}_2$  and 25 g. NaCl (to assist in solution) per liter. It is equivalent to the potassium iodide solution volume for volume. It is best made up by weighing out a slight excess of the salt, then standardizing against the potassium iodide solution and diluting to the proper strength.
7. Potassium permanganate, 0.5 g. per liter.
8. Barium acetate, 10%, in 30% alcohol by volume.

The complete method of analysis follows. The directions are the same as given by Pratt, except where the present modifications enter in.

Throw out the pectins by adding twice the volume of 50% alcohol. When the precipitate has settled, filter through paper on a Büchner funnel, and wash twice with 65% alcohol, sucking the gelatinous precipitate as dry as possible. Dilute the filtrate with water to give approximately a 30% alcohol content by volume and add slowly 5 cc. of the barium acetate solution. When the barium citrate has settled to the bottom, filter through asbestos in a Gooch, wash once with 30% alcohol, and dry in a water oven. The barium citrate is next dissolved with hot 6% phosphoric acid solution, using three portions of 20 cc. each, and followed by hot water. The filtrate and washings should be about 100 cc. They are transferred to the oxidation flask and the latter connected with a spiral condenser and with the device for adding potassium permanganate. To prevent bumping, introduce into the flask a piece of glass tubing sealed at the upper end, and long enough to remain upright. Sometimes a few glass beads are also necessary. The adapter of the condenser dips into 40 cc. of Denigès' solution contained in a 500 cc. Erlenmeyer flask. Heat the citrate solution over a naked flame, then allow the permanganate to drop into the briskly boiling solution at the rate of 20 to 25 drops in 10 seconds. When a deep pink color has persisted for a couple of minutes the reaction is complete. If the volume of liquid in the flask becomes too small, successive portions of 20 cc. of water may be added, care being taken to shut off the flow of per-

manganate a few moments before the distillation is stopped and the system is opened. The distillate is made up to 300 cc., put under a reflux condenser and boiled gently for 45 minutes. If the distillate is over 300 cc., more Denigès' solution should be added at the rate of 15 cc. for each 100 cc. of distillate in excess of 300 cc.

The precipitate is filtered hot through paper, washed by decantation twice with hot water, then the filter paper washed thoroughly. The precipitate in the Erlenmeyer is dissolved in two or three small portions of 5% HCl by heating, each portion being poured through the filter containing the rest of the precipitate and collected in a 100 cc. flask. The acid solution is returned through the filter till all precipitate is dissolved. After thoroughly washing the filter and flask with hot water, the filtrate is cooled, very nearly neutralized with 10% sodium hydroxide, and made up to 100 cc. The mercury can now be titrated by either one of the two following methods: (a) The whole or an aliquot of the mercury solution can be poured into an excess of the potassium iodide solution, and the excess potassium iodide titrated back with the standard mercuric chloride solution. The amount of potassium iodide solution necessary for the whole sample can then be calculated, together with the citric acid equivalent. (b) The mercuric chloride solution under examination can be placed in a buret and titrated directly against say, 10 or 15 cc. of the standard potassium iodide, and the amount of citric acid in the whole sample computed. For amounts of citric acid of 100 mg. or over, (b) is the preferable procedure. If (a) is used, the aliquot used should not be less than one-fourth.

Malic, tartaric (except quantities of 0.5 g. or over), oxalic, and aconitic acids do not interfere with this determination. The presence of much sugar, or other substances capable of reducing permanganate, tends to give slightly high results, but the difference is inconsiderable.

TABLE IV.

The Analysis of Certain Plant Products for Citric Acid.

The author with modified method.		A. O. A. C. collaborators with Pratt's method, using orange juice titrating 0.83 % citric acid.			
Substance analyzed.	Citric acid.	Collaborator.	Citric acid.	Collaborator.	Citric acid.
Sorghum syrup.....	$\left\{ \begin{array}{l} 0.599\% \\ 0.586 \end{array} \right.$	J. M. J....	$\left\{ \begin{array}{l} 0.79\% \\ 0.89 \end{array} \right.$	P. B. D....	$\left\{ \begin{array}{l} 0.72 \\ 0.73 \end{array} \right.$
Lemon juice, titrating 6.64% citric acid...	$\left\{ \begin{array}{l} 6.69 \\ 6.64 \end{array} \right.$		$\left\{ \begin{array}{l} 0.79 \\ 0.76 \\ 0.84 \end{array} \right.$		$\left\{ \begin{array}{l} 0.63 \\ 0.72 \\ 0.69 \end{array} \right.$
Grapefruit juice, titrating 0.90% citric acid	$\left\{ \begin{array}{l} 0.976 \\ 0.993 \end{array} \right.$	P. A. Y....	$\left\{ \begin{array}{l} 0.824 \\ 0.836 \\ 0.787 \\ 0.840 \end{array} \right.$	H. C. G....	$\left\{ \begin{array}{l} 0.81 \\ 0.80 \\ 0.73 \\ 0.87 \\ 0.80 \\ 0.84 \end{array} \right.$

In order to show the accuracy of duplicate determinations by the modified method, several products were analyzed for citric acid. The results are shown in Table IV. For the sake of comparison, the table of results given in the 1912 report of the A. O. A. C. is also reproduced.

These results seem to warrant the conclusion that the modified method, if followed rigidly, will give much more satisfactory results than the original one. It is hoped that other workers will give the proposed method a trial, as a trustworthy method for determining citric acid in plant products is needed.

DIVISION OF AGRICULTURAL BIO-CHEMISTRY  
UNIVERSITY OF MINNESOTA.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY,  
No. 281.]

## AN EXAMINATION OF CERTAIN METHODS FOR THE STUDY OF PROTEOLYTIC ACTION.

By H. C. SHERMAN AND DORA E. NEUN.

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There is no lack of methods for the study of proteolytic action but, in general, each method has been devised to meet the needs of a particular line of investigation, or to determine whether or not a commercial pepsin or trypsin complies with the standard arbitrarily established for it. As a preliminary to research upon the proteases, it seemed desirable to study some of these methods with reference to their accuracy and delicacy and their adaptability to proteases of more than one type. The methods studied were: The determination of total digested nitrogen, the increase of amino nitrogen as measured by the Van Slyke method, the acidimetric titration of digestion products, the change in electrical conductivity, and in rotation of polarized light, the Mett method, and the biuret and ninhydrin reactions. The work of Long and Barton<sup>1</sup> published soon after the present investigation was begun, made it unnecessary for us to include certain other well-known methods in our comparison. We have used commercial pepsins and trypsins of good quality and have arranged our experiments with a view to ascertaining to what extent the various methods will permit comparisons of these two types with each other. In the following pages typical results obtained by each of the methods tested are presented very briefly, the work on the ninhydrin reaction being further abbreviated in view of the investigations of Van Slyke and his associates<sup>2</sup> and of Harding and MacLean,<sup>3</sup> the results of which have become available while our studies were in progress.

<sup>1</sup> THIS JOURNAL, 36, 2151 (1914).

<sup>2</sup> *Proc. Soc. Expt. Biol. Med.*, 11, 154 (1914); *J. Am. Med. Assoc.*, 65, 945 (1915); Harvey Society Lectures, 1915-16.

<sup>3</sup> *J. Biol. Chem.*, 20, 217 (1915); 24, 503 (1916); 25, 319, 337 (1916).

### Mett Method.

This method which has long been popular because of the convenience of observing results, and which is the only one in which we have used egg white as substrate, may be described first.

Utilizing the improvements proposed by Cobb<sup>1</sup> and introducing slight modifications in the interest of greater accuracy, we have carried out this method as follows:

Glass tubing of 2.5 to 3 mm. bore is cut into 20 cm. lengths and washed successively with cleaning mixture, water, alcohol, and ether. The ends are then drawn to a capillary and broken off. The white of a fresh egg is thoroughly cut with scissors, filtered through cheesecloth, placed under vacuum for an hour to eliminate air and prevent the subsequent formation of air bubbles, and then sucked up into the prepared glass tubes and the ends of the latter sealed by fusing. The egg-white is coagulated by immersing the tubes in water heated at 95°. In doing this the tubes are laid horizontally upon a wire gauze about 1 cm. below the surface of the water, the temperature of 95° is maintained for 15 minutes after the introduction of the tubes, then the source of heat is removed and the whole allowed to stand until the water is cold, lest by cooling too rapidly a large part of the tube be rendered useless by retraction of the egg-white from the glass walls. In view of the experience of Nirenstein and Schiff,<sup>2</sup> we have always used tubes less than three days old. In making the digestion test, 20 cc. portions of the solution of pepsin in 0.05 *M* HCl<sup>2</sup> (or of trypsin in 0.05 *M* Na<sub>2</sub>CO<sub>3</sub><sup>3</sup>) were placed in flat bottomed cylindrical jars of 5 to 6 cm. diameter, the depth of the solution being thus about 1 cm.; the tubes of coagulated egg-white were cut into 2 cm. lengths with smooth, square ends, and two of these lengths immediately placed in each of the jars containing the enzyme solutions and the whole enclosed in a thermostat kept at 40°. At the end of the 20 hours allowed for the digestion test the tubes were removed and the length of column digested was measured four times at each end of both tubes, making 8 measurements on each tube or 16 measurements on the pair of tubes by which each enzyme solution was tested. These measurements were made under a microscope fitted with a mechanical stage and vernier (Leitz No. 141) and a micrometer eyepiece. Under these conditions it is believed that the error in case of pepsin digestions should never be greater than 0.1 mm. in any one reading<sup>4</sup> and that the average of the 16 readings taken for each enzyme solution is reasonably accurate to the second decimal place (expressed in mm.). It is this final average of 16 measurements which appears under the heading of "column digested" in Table I.

In the case of pepsin the Mett method with digestion for 20 hours at 40°, permitted measurements of activity of as little as 2 parts of the commercial enzyme in 1,000,000 of the test solution or 0.04 mg. in the 20 cc. used for a test, thus showing a fairly high degree of delicacy. For quantitative comparisons, however, this method is open to the objection that the observed result of the enzyme action increases only very slowly with the amount of enzyme present, unless this amount be very small. This is

<sup>1</sup> *Am. J. Physiol.*, 13, 448 (1905).

<sup>2</sup> *Arch. f. Verdauungskrankh.*, 8, 599 (1903).

<sup>3</sup> These being the concentrations of acid and alkali which in our experience are most favorable to the activity of pepsin and trypsin, respectively.

<sup>4</sup> In trypsin digestions the alkalinity of the solution affects the surface of coagulated eggwhite and greatly increases the error in the reading as explained beyond.



TABLE I.—RESULTS OF EXPERIMENTS BY THE METT METHOD (20 HOURS).  
Column digested (in millimeters).

Concentration.	Enzyme in test solution. Wt. (mg.).	Pepsin I.	Pepsin II.	Pepsin III.	Trypsin II.
25 : 1000	500	....	....	....	3.5
16 : 1000	320	....	....	....	2.8
9 : 1000	180	7.26	6.64	7.14	2.1
4 : 1000	80	5.32	5.31	6.04	1.1
3 : 1000	60	....	....	....	0.4
2 : 1000	40	....	....	....	0.0
1 : 1000	20	3.28	3.37	3.89	...
1 : 2000	10	2.53	2.57	(4.04)	...
1 : 4000	5	2.02	1.96	2.50	...
1 : 8000	2.5	1.44	1.51	1.84	...
1 : 16000	1.25	0.98	....	....	...
1 : 32000	0.625	0.63	....	....	...
1 : 64000	0.312	0.40	....	....	...
1 : 128000	0.156	0.15	....	....	...
1 : 256000	0.078	0.11	....	....	...
1 : 512000	0.039	0.05	....	....	...
Blank	None	0.00	0.00	0.00	...

shown by the data of Table I and perhaps more clearly by the curves in Fig. 1. Here the upper solid line (A), which on the scale here used appears nearly vertical, is what would represent a direct linear relationship between the amount of pepsin present and length of column digested. Curve B represents the square root relationship predicated by the Schütz-

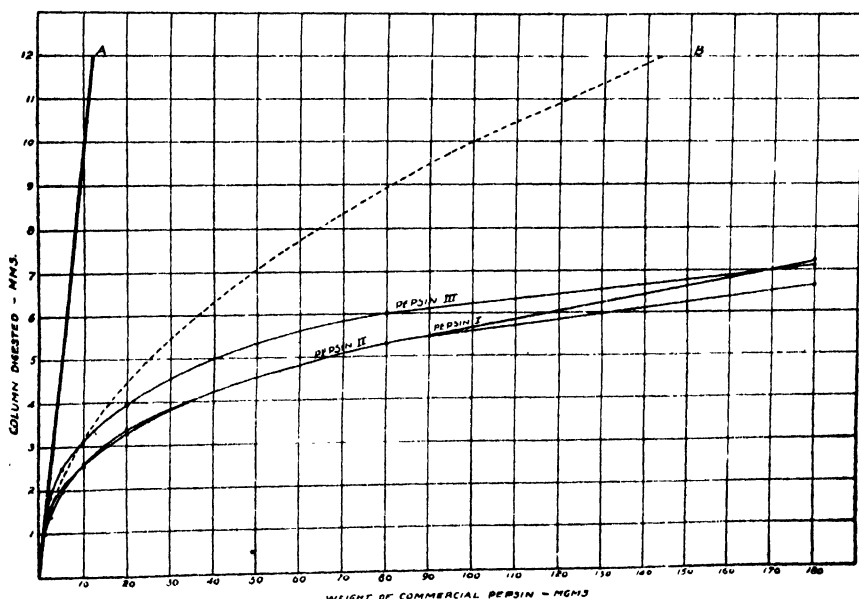


FIG. 1.—Comparison of (A) linear relationship, (B) square-root relationship, with results shown by Mett method in testing three commercial preparations of pepsin.

Borissow rule,<sup>1</sup> and Curves I, II, and III show the results actually obtained with the three pepsins represented in Table I.

Our results like those of Nirenstein and Schiff<sup>2</sup> and of Cobb<sup>2</sup> indicate that the Schütz-Borissow rule fails before the pepsin reaches a sufficient concentration to digest 4 mm. of the column in 20 to 24 hours. With increasing concentrations of enzyme the discrepancy increases rapidly. Taking the best result obtained among the three pepsins tested, 80 mg. actually digested only as much as should have been digested by 36 mg. according to the Schütz-Borissow square root rule, or as would be digested by 6 mg. if the observed result were in direct arithmetical proportion to the amount of enzyme present, which is obviously the desired relationship in quantitative testing of enzymes and is very nearly realized in the testing of amylases and in some of the methods available for testing proteases as will appear below. In Fig. 2 the results obtained with the smaller

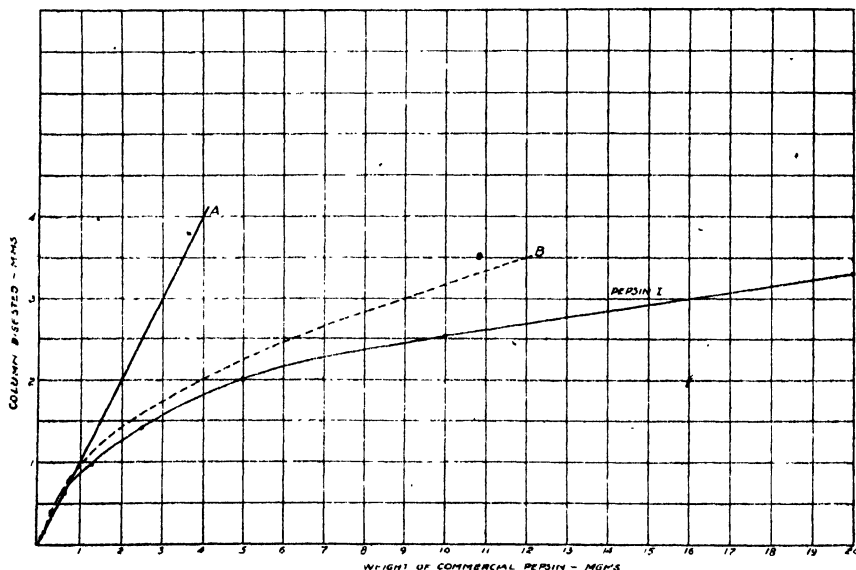


Fig. 2.—Comparison of linear and square-root relationships with results shown by Mett method in testing very small amounts of pepsin.

amounts of Pepsin I are plotted in the manner of Fig. 1, but on a larger scale in order to permit observations of the relationships in low concentrations of enzyme. Here it will be seen that the curve of actual results and the two "theoretical" curves are hardly distinguishable during the first millimeter of digestion but that to digest two millimeters, which in the case of a linear relationship would require 2 mg. and according to the square

<sup>1</sup> E. Schütz, *Z. Physiol. Chem.*, 9, 577 (1885); J. Schütz, *Ibid.*, 30, 1 (1900).

<sup>2</sup> *Loc. cit.*

root rule should have required 4, actually required 5 mg.; while 10 mg. actually accomplished only what should have been done by 6.5 mg., according to the square root rule.

Hence it appears that the observed result in this method is approximately proportional to the amount of pepsin only at the very lowest concentrations with which of course the length of column digested is too short for any high degree of accuracy in measurement.

With trypsin all the measurements are likely to be inaccurate, because the alkali of the solution acts upon the coagulated albumin, causing a jelly-like meniscus which is very difficult to read. Moreover, the results show plainly that this method is not well adapted to the study of trypsin because egg albumin, even when coagulated, is a relatively resistant substrate for this enzyme.

#### Casein Substrate for all Following Methods.

In all of the experiments hereinafter described, casein<sup>1</sup> was used as substrate. For pepsin digestions the casein was suspended in 0.05 *M* HCl. For trypsin digestions solutions of sodium caseinate, of the slight alkalinity best suited to tryptic activity, were prepared as follows:

Ten grams of casein were dissolved in a mixture of about 200 cc. of distilled water and 8 cc. of molar sodium hydroxide. The mixture was slowly heated to 40° to aid solution and then rapidly heated to 85–90° to destroy any traces of proteolytic enzyme which might be contained in the casein. The solution was cooled and made up to 500 cc. For each determination, 50 cc. of this solution were placed in a 100 cc. flask, diluted to about 90 cc., warmed to 40° in a thermostat, constant to 0.01°, the enzyme added, and the volume made up to 100 cc. During the digestion the flasks were protected from the rays of light from the lamps in the thermostat. The enzyme action was stopped at stated intervals by pouring the digestion mixture (100 cc.) into 25 cc. of 20% sodium sulfate solution and then adding 5 cc. of half-molar hydrochloric acid. After standing for an hour, the undigested casein was filtered off and aliquot portions of the filtrate used for the measurement of proteolysis by the various methods already mentioned, such as titration, amino nitrogen, total nitrogen, etc.

In the pepsin experiments, 1 g. of casein was weighed out for each flask and dissolved in 0.05 *M* hydrochloric acid, the solution warmed, enzyme added and the volume made up to 100 cc. At the end of the digestion period, the undigested casein was precipitated by pouring the digestion mixture into 25 cc. of 20% sodium sulfate solution. After standing one hour, the casein was filtered out and portions of the filtrate analyzed as in the case of trypsin.

#### Total Nitrogen of Digestion Products.

In the filtrate obtained after precipitation of undigested casein by sodium sulfate and hydrochloric acid as described above, nitrogen can readily be determined by the Kjeldahl method and thus a measure obtained of the total of digestion products which have passed the early proteose stage. In using this as a method of studying proteolytic action of enzymes, "blank tests," in which all conditions and manipulations are the same except for the addition of the enzyme, must always be made and the nitro-

<sup>1</sup> Kahlbaum's "Casein nach Hammarsten."

gen thus found deducted. When relatively large amounts of enzyme preparation are used the soluble nitrogen thus introduced must also be allowed for. The figures given in the tables which follow are in all cases for the nitrogen found in the filtrates *in excess* of that found in the "blank." Table II shows the amounts of nitrogen digested by different weights of commercial pepsins and trypsins acting for a fixed length of time. Table III shows the results of a fixed weight of enzyme acting for different lengths of time.

TABLE II.—TOTAL NITROGEN OF DIGESTION PRODUCTS FORMED BY DIFFERENT WEIGHTS OF ENZYMES ACTING UPON 1 G. OF CASEIN IN A DIGESTION MIXTURE OF 100 CC. AT 40°.

Mg. of commercial enzyme.	Half-hour digestions.		20-hour digestions.	
	Pepsin I. Mg. of nitrogen digested.	Trypsin I. Mg. of nitrogen digested.	Pepsin I. Mg. of nitrogen digested.	Trypsin I. Mg. of nitrogen digested.
0.001	0.2	0.2	0.5	1.4
0.002	0.7	0.6	1.8	2.2
0.01	0.9	0.9	7.0	9.1
0.05	1.7	1.7	23.8	41.6
0.1	3.0	3.3	37.9	71.9
0.5	9.6	13.6	65.3	132.5
1	19.3	28.3	89.8	133.2
2	30.2	55.2	96.5	134.1
5	51.1	97.6	106.9	133.5
25	93.3	132.9	117.4	134.0
50	(89.2)	133.6	114.0	135.2
100	109.7	133.4	121.9	135.3

TABLE III.—TOTAL NITROGEN OF DIGESTION PRODUCTS.

Amounts Formed in Different Times by 1 Milligram of Enzyme Acting on 1 Gram of Casein at 40°.

Time of digestion. Hours.	Pepsin I. Mg.	Trypsin I. Mg.	Trypsin II. Mg.	Apparent value of Trypsin I in percentage of that of Trypsin II as affected by time of digestion.
1/2	19.8	36.1	16.6	217
1	31.2	61.4	32.0	192
2	44.4	98.4	59.5	165
3	55.6	119.1	81.9	145
4	62.3	128.4	100.3	128
6	73.9	133.4	120.2	111
8	79.8	135.8	128.4	106
21	97.4	138.4	136.5	101
48	107.4	138.0	136.4	101

Comparing the delicacy of this method as shown by the data of Table II with that of the Mett method as shown in Table I, we find that in 20-hour digestions with Pepsin I the smallest amount of this commercial enzyme which was demonstrable by the Mett method was about 0.04 mg., while by the present method 0.001 mg. could be demonstrated with an equal degree of certainty and 0.01 mg. gave a yield of digestion products

sufficient for fairly accurate quantitative measurement. With trypsin, to which the Mett method has been seen to be poorly adapted, the present method gives excellent results. In the case of the commercial enzymes here used the present method permitted positive demonstration of trypsin at quite as great dilution as of pepsin and with increasing amounts of enzyme in the digestion mixtures the trypsin showed regularly higher proteolytic values than did equal weights of the pepsin obtained from the same manufacturer at the same time.<sup>1</sup>

The value of this method for quantitative comparisons is shown by the fact that, allowing for the probable errors of experiment, the amount of digested nitrogen increases in direct proportion to the amount of enzyme used up to about 20–25 mg. of nitrogen in the case of pepsin, or 40–60 mg. of nitrogen in the case of trypsin, quantities large enough to be determined by the Kjeldahl method with a high degree of accuracy.

A comparison of the data for Trypsins I and II in Table III illustrates the importance of avoiding too long a time (or too large a quantity of enzyme) in making comparisons of enzyme activities. Trypsin I has about twice the activity of Trypsin II, as may be seen by comparing the amounts of total digested nitrogen for 30 minutes or for 1 hour of digestion. But when the digestion is too prolonged the product of the weaker enzymes steadily approaches that of the stronger until at the end of 8 hours the enzyme which really has twice the activity appears but little more active. If, on the other hand, we compare the lengths of time required to digest a given amount of nitrogen, we find that, up to quite high amounts, the times required by Trypsin I and Trypsin II are approximately as 1 : 2. This may be seen by reference to the data of Table III, or (perhaps better), the curves in Fig. 4, from which it will be seen that the production of any given amount of total digested nitrogen (even up to 128 mg.) requires almost exactly twice as long with Trypsin II as with Trypsin I.

#### Amino Nitrogen of Digestion Products (Van Slyke Method).

In our experiments with this method, 2 cc. portions of the filtrates obtained as already described, which contained the digestion products formed by the action of pepsin or trypsin on casein, were analyzed for amino nitrogen by the Van Slyke method<sup>2</sup> in the "micro" apparatus, using the new 3 cc. gas buret recently described. Our experience leads us to emphasize the importance of frequent "reagent blank" determinations in order to

<sup>1</sup> It should, however, be noted in this connection that the commercial pepsin contained only 2.25% of nitrogen while the commercial trypsin contained 10.95% of nitrogen. Undoubtedly considerable amounts of inert material were present in both samples. It cannot be inferred that the digestive activities of pure pepsin and pure trypsin would bear the same quantitative relation to each other as do these commercial products. On the other hand, the commercial products used in our experiments have as high proteolytic activity as any which we have yet found in the market.

<sup>2</sup> *J. Biol. Chem.*, 9, 185 (1911); 12, 275 (1912); 16, 121 (1913); 23, 407 (1915).

detect deterioration of any of the substances used, especially the caprylic or heptyl alcohol which is introduced to prevent frothing. The determinations were carried out in all respects as described by Van Slyke, and the amounts of amino nitrogen found in the 2 cc. portions of filtrate were corrected for "blank" then multiplied by 62.5 or 65 to obtain the total amino nitrogen formed<sup>1</sup> by the action of the enzyme in each case. The data so obtained are given in Table IV.

TABLE IV.—AMINO NITROGEN (MEASURED BY VAN SLYKE METHOD) FORMED BY DIFFERENT WEIGHTS OF ENZYME ACTING UPON 1 GRAM OF CASEIN AT 40°.

Mg. of commercial enzyme.	Half-hour digestions.		20-hour digestions.	
	Pepsin I.	Trypsin I.	Pepsin I.	Trypsin I.
	Mg. of amino nitrogen.	Mg. of amino nitrogen.	Mg. of amino nitrogen.	Mg. of amino nitrogen.
0.001	0.0	0.0	0.0	0.5
0.002	0.0	0.0	0.2	0.7
0.01	0.0	0.0	0.3	1.3
0.05	0.0	0.0	1.7	4.6
0.1	0.2	0.7	3.3	8.1
0.5	0.7	2.0	5.5	21.0
1	1.5	3.3	7.0	26.7
2	3.0	5.4	9.4	31.3
5	4.6	11.0	11.9	36.1
25	8.9	27.1	14.8	44.9
50	11.2	35.1	15.8	50.2
100	14.1	41.0	17.8	58.2

If the data of Table IV, especially those for the very small amounts of enzyme, be compared in detail they appear somewhat irregular, probably because of the multiplication of unavoidable errors of observation by the large factor (62.5 or 65). The general trend of the results is, however, quite regular, as may be seen from Fig. 3, where the total and amino nitrogen of the products of half-hour digestions are shown together. The amino nitrogen formed in a given experiment is of course much smaller in amount than the total nitrogen of digestion products (unless the experiment be pushed far beyond the limits of those here considered) and after all of the casein has been converted into digestion products and the total nitrogen of digestion products can no longer increase, the amino nitrogen continues to rise as the proteoses, peptones and peptids are split to yield amino acids. Hence this method, in addition to measuring a change which is more definite in its chemical nature, has also the advantage of enabling one to follow the later stages of proteolysis. On the other hand, the very first stages of proteolysis are more readily detected by determining the total nitrogen of digestion products.

The amino nitrogen of digestion products was also determined in the

<sup>1</sup> The enzyme acts in a volume of 100 cc., but the sulfate solution and standard acid added at the end of the digestion period bring the total volume to 130 cc. in the case of trypsin experiments and 125 cc. in the case of pepsin.

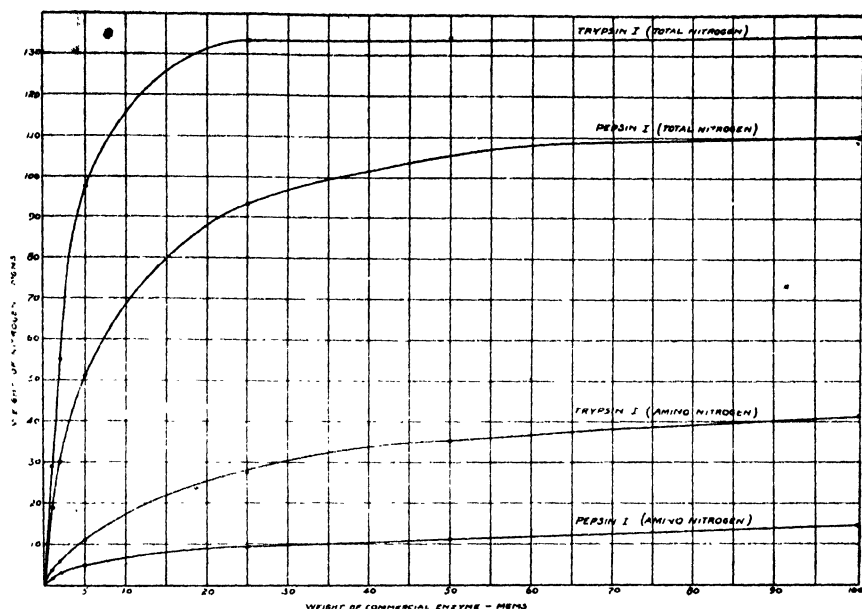


Fig. 3.—Comparison of activity of Pepsin I and Trypsin I as shown by total nitrogen of digestion products (upper two curves), and by increase of amino nitrogen (lower two curves).

experiments (of which the total nitrogen of digestion products was shown in Table III) in which fixed amounts of enzyme were allowed to act for different lengths of time. The results thus obtained are shown in Table V, and those for the trypsins graphically in Fig. 4. As would be expected, the amino nitrogen of digestion products continues to increase long after the total nitrogen of digestion products has reached its maximum and is, therefore, applicable to the study of much later stages of the digestion. Comparing the two trypsins, I and II, we find them bearing the same relation to each other here as in Table III. The results of the determination of both total and amino nitrogen for digestion products of Trypsins I and II at different time intervals are shown together in Fig. 4.

TABLE V.—AMINO NITROGEN OF DIGESTION PRODUCTS (VAN SLYKE METHOD).  
Amounts Formed in Different Times by 1 Mg. of Enzyme Acting  
on 1 G. of Casein at 40°.

Time of digestion. Hours.	Pepsin I. Mg.	Trypsin I. Mg.	Trypsin II. Mg.	Time of digestion. Hours.	Pepsin I. Mg.	Trypsin I. Mg.	Trypsin II. Mg.
1/2	0.71	3.02	1.48	8	6.12	22.00	17.41
1	1.56	6.50	2.98	21	8.93	25.71	24.53
2	3.17	10.85	6.01	48	10.55	29.55	29.47
3	3.82	14.10	9.39	72	10.60 <sup>1</sup>	31.84	.....
4	4.53	17.25	11.23	120	11.08 <sup>1</sup>	33.70	.....
6	5.23	19.63	14.34	168	12.31 <sup>1</sup>	35.61	.....

<sup>1</sup> These solutions contained thymol as antiseptic.

Here again we find striking evidence of the importance of reasonably short digestion periods in comparing the activities of two enzyme preparations. As already explained and as shown by the figures for 30 minutes' or for 1 hour's digestion as given in Table V, the activity of Trypsin I is about twice that of Trypsin II, but when the length of the digestion period is prolonged the difference between the two samples appears less

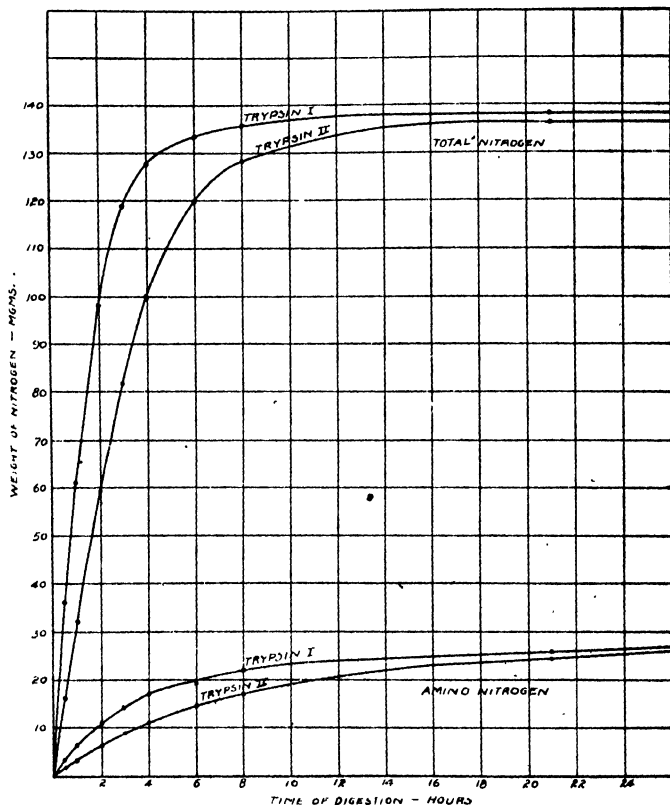


Fig. 4.—Comparison of activities of Trypsins I and II as measured by total nitrogen of digestion products (upper two curves) and by increase in amino nitrogen due to action of enzyme on substrate (lower two curves).

and less and by the end of about 20 hours they appear to be equally active. Thus in a comparison in which the time of digestion is too long a difference of 100% in the activity of two enzyme preparations may be entirely obscured. Unless the amount of protease present is exceedingly minute or the proteolytic activity very feeble the time of digestion should be preferably not be longer than 30 minutes or one hour.

If, instead of comparing the products obtained in a given length of time, one compares the length of time required for the formation of a given



amount of the product, the true relative values of the two trypsin can be traced through longer periods of time and to larger yields of product. Thus 14 mg. of amino acid nitrogen were formed by Trypsin I in three hours, by Trypsin II in six hours; 17 mg. of amino acid nitrogen required in the case of Trypsin I four hours, of Trypsin II eight hours. Even in this case, however, very long periods would be apt to give seriously misleading results, because when the reaction has become very slow the unavoidable errors in determining the total product would necessarily be large as compared with the small hourly increment.

#### Titration of Acid Cleavage Products (Volhard-Löhlein Method).

Thomas and Weber<sup>1</sup> estimated the activity of trypsin by allowing it to act upon casein as in the general procedure above described and weighing the undigested casein precipitated at the end of the digestion period. Volhard<sup>2</sup> tested pepsin, and Löhlein<sup>3</sup> trypsin, by titrating the filtrate. In 1912, Miss Ruth, working with one of us, obtained promising results from this method and we have therefore included it in the present comparison.

In most of the above experiments for which the total nitrogen or amino nitrogen of the filtrate has been determined, a portion of the filtrate (usually 50 cc.) has been titrated with tenth-molar sodium hydroxide with thymolphthalein as indicator. The amount of alkali thus required, above that required in the "blank," depends upon the carboxyl groups of the digestion products plus a little of the hydrochloric acid used in the digestion or added with the sulfate solution to precipitate the undigested casein; for the acidity of the "blank" filtrate does not account for all of the hydrochloric acid which was added, indicating that some of it is held by the undigested casein. In the pepsin tests this hydrochloric acid is liberated as the digestion proceeds. In the trypsin tests the more complete the digestion of the casein, the less hydrochloric acid will it hold when precipitated at the end of the digestion period. The fact that this method measures something more than the liberation of amino acids suggested that it might yield information somewhat different from that obtained from the Van Slyke and Sørensen methods.<sup>4</sup> In so far as it depends upon the titration of carboxyl groups, it is particularly appropriate that this method should accompany the use of casein as substrate on account of the high proportion of dibasic monoamino acid shown by Osborne and others to result from the hydrolysis of casein.<sup>5</sup>

<sup>1</sup> *Centrbl. f. Stoffw.-u. Verd.-Krankh.*, 2, 365 (1901).

<sup>2</sup> *Biochem. Z.*, 2, 231 (1903).

<sup>3</sup> *Beitr. Chem. Physiol.-Path.*, 7, 120 (1905).

<sup>4</sup> We have accepted the results of Harding and MacLean (*Loc. cit.*) as sufficiently indicative that the results of the Sørensen method run parallel with those of the Van Slyke and so have not included the Sørensen method in our comparative experiments.

<sup>5</sup> Osborne and Guest, *J. Biol. Chem.*, 9, 352 (1911).

The results obtained by this method are shown in Tables VI and VII, where (as in the preceding tables) the figures given are in all cases calculated for the total solution so as to indicate the work done by the amount of enzyme stated. Some of the filtrates were opalescent, making the end point of the titration somewhat uncertain. This method appears somewhat less delicate than the determination of total nitrogen; about as delicate but not so regular in its results as the determination of amino nitrogen in the filtrate. It is about equally delicate for pepsin and trypsin (referring of course to the commercial preparations here used), so that in 20-hour digestions both can be detected with certainty when present in quantities of 0.01 mg. and usually when as little as 0.002 mg. is present.

TABLE VI.—ACIDITY OF CLEAVAGE PRODUCTS (VOLHARD-LÖHLEIN METHOD) FORMED BY ACTION OF DIFFERENT WEIGHTS OF COMMERCIAL ENZYMES UPON 1 G. OF CASEIN AT 40°.

Mg. of commercial enzyme.	Half-hour digestions.		20-hour digestions.	
	Pepsin I.	Trypsin I.	Pepsin I.	Trypsin I.
	Acidity over that of "blank,"		in terms of cc. 0.1 M NaOH.	
0.001	0.0	0.0	0.0	0.2
0.002	0.1	0.0	0.1	0.2
0.01	0.1	0.0	0.6	1.2
0.05	0.2	0.0	2.4	5.8
0.1	0.3	0.6	4.2	11.0
0.5	0.9	1.3	8.5	22.5
1	1.9	3.0	12.1	26.0
2	3.3	6.1	13.1	27.7
5	6.1	12.1	15.3	30.1
25	12.3	25.6	18.5	33.9
50	12.4	28.6	18.7	35.6
100	16.0	30.6	21.1	37.8

TABLE VII.—ACIDITY OF DIGESTION PRODUCTS RESULTING FROM ACTION OF 1 MG. OF COMMERCIAL ENZYME UPON 1 G. OF CASEIN FOR DIFFERENT LENGTHS OF TIME AT 40°.

Time of digestion. Hours.	Acidity over that of "blank"—cc. of 0.1 M NaOH.		
	Pepsin I.	Trypsin I.	Trypsin II.
1/2	1.75	4.43	2.02
1	2.83	8.18	4.10
2	4.50	13.58	7.81
3	5.83	18.00	10.83
4	6.75	19.56	14.37
6	8.58	22.81	18.40
8	9.33	23.98	21.52
21	12.25	26.20	25.80

The general trend of these results (Tables VI and VII) is very nearly parallel with that for the total nitrogen of digestion products (Tables II and III). While the determination either of total, or of amino, nitrogen of digestion products is preferable both in delicacy and on theoretical

grounds, the convenience of this titration method makes it worthy of further study as a rapid approximate method for the measurement of proteolytic action.

### The Increase of Electrical Conductivity.

In view of the prominence given by Bayliss<sup>1</sup> to the conductivity method in his study of tryptic action, we have determined the increase of electrical conductivity resulting from the action of different amounts of trypsin upon casein substrates prepared in the manner already described. In this work the spiral Kohlrausch bridge of Leeds and Northrup was used with telephone buzzer. The solutions were contained in Freas conductivity cells having electrodes about 1 cm. square and about 1 cm. apart. The results of typical experiments are shown in Table VIII. Experiments were also made in which the enzyme was allowed to act upon the substrate in a conductivity cell, so arranged that determinations of conductivity could be made from time to time without interruption of the digestion. Table IX shows the results of a typical experiment of this type.

TABLE VIII.—INCREASE IN ELECTRICAL CONDUCTIVITY RESULTING FROM ACTION OF DIFFERENT WEIGHTS OF COMMERCIAL TRYPSIN UPON CASEIN SUBSTRATE AT 40°.

Mg. of commercial enzyme.	Increase in reciprocal ohms.			
	Half-hour digestions.		20-hour digestions.	
	Trypsin I. (1) <sup>2</sup>	Trypsin II. (2) <sup>2</sup>	Trypsin I. (3) <sup>2</sup>	Trypsin II. (4) <sup>2</sup>
0.002	0.00	0.00	0.00	0.00
0.01	0.00	0.00	0.16 × 10 <sup>-4</sup>	0.00
0.05	0.04 × 10 <sup>-4</sup>	0.00	0.47 × 10 <sup>-4</sup>	0.10 × 10 <sup>-4</sup>
0.1	0.07 × 10 <sup>-4</sup>	0.12 × 10 <sup>-4</sup>	0.81 × 10 <sup>-4</sup>	0.29 × 10 <sup>-4</sup>
0.5	0.21 × 10 <sup>-4</sup>	0.18 × 10 <sup>-4</sup>	2.26 × 10 <sup>-4</sup>	1.24 × 10 <sup>-4</sup>
1	0.37 × 10 <sup>-4</sup>	0.25 × 10 <sup>-4</sup>	3.03 × 10 <sup>-4</sup>	1.62 × 10 <sup>-4</sup>
2	0.66 × 10 <sup>-4</sup>	0.40 × 10 <sup>-4</sup>	3.44 × 10 <sup>-4</sup>	2.37 × 10 <sup>-4</sup>
5	1.26 × 10 <sup>-4</sup>	0.84 × 10 <sup>-4</sup>	3.99 × 10 <sup>-4</sup>	3.91 × 10 <sup>-4</sup>
100	5.58 × 10 <sup>-4</sup>	....	11.62 × 10 <sup>-4</sup>	....
250	8.82 × 10 <sup>-4</sup>	....	15.65 × 10 <sup>-4</sup>	....

This method is very convenient (as Bayliss has previously shown) for following the time curve of tryptic digestions, but offers no special advantage in comparing the effects of different amounts of enzyme. For the purposes of our investigations it has seemed preferable on theoretical grounds to depend chiefly upon those methods in which the effect measured can be expressed in definite chemical terms, *viz.*, as total nitrogen or as amino nitrogen of digestion products formed by the action of the enzyme.

<sup>1</sup> *Arch. d. Sciences Biologiques*, 11, 261 (1904); *J. Physiol.*, 36, 221 (1907).

<sup>2</sup> Conductivity of "blanks" solutions: (1) 6.54 × 10<sup>-4</sup>; (2) 6.48 × 10<sup>-4</sup>; (3) 6.72 × 10<sup>-4</sup>; (4) 6.48 × 10<sup>-4</sup>.

TABLE IX.—INCREASE OF ELECTRICAL CONDUCTIVITY RESULTING FROM ACTION OF  
1 MILLIGRAM OF COMMERCIAL TRYPSIN UPON 1 GRAM OF CASEIN  
SUBSTRATE FOR DIFFERENT LENGTHS OF TIME AT 40°.

Time of digestion. Hours.	Increase of conductivity of digesting solution.	
	Trypsin I (1). <sup>1</sup> Reciprocal ohms.	Trypsin II (2). <sup>1</sup> Reciprocal ohms.
$\frac{1}{2}$	$0.30 \times 10^{-4}$	$0.24 \times 10^{-4}$
1	$0.63 \times 10^{-4}$	$0.54 \times 10^{-4}$
2	$1.06 \times 10^{-4}$	$0.80 \times 10^{-4}$
3	$1.23 \times 10^{-4}$	$1.02 \times 10^{-4}$
4	$1.36 \times 10^{-4}$	$1.21 \times 10^{-4}$
5	$1.51 \times 10^{-4}$	$1.33 \times 10^{-4}$
6	$1.61 \times 10^{-4}$	$1.46 \times 10^{-4}$
7	$1.75 \times 10^{-4}$	$1.56 \times 10^{-4}$
9	$2.06 \times 10^{-4}$	$1.76 \times 10^{-4}$
24	$3.22 \times 10^{-4}$	$2.95 \times 10^{-4}$

### The Polariscopic Method.

Most investigators who have employed the optical method for the study of proteolysis have made use of an optically active di-, tri-, or poly-peptid as substrate. Abderhalden<sup>2</sup> tests for proteolytic action by polariscopic observations upon mixtures of blood serum and peptone prepared from tissue protein. In order to test the usefulness of this method for studies of the action of enzymes on typical protein, we have examined portions of the digestion filtrates obtained as described in connection with the four preceding methods, in comparison with those of the "blank" tests to determine what, if any, change had occurred in the optical rotatory effect of the substrate solution as the result of the action of the enzyme. A very delicate polariscope,<sup>3</sup> reading to hundredths of an angular degree, was employed. Readings were usually made in a 220 mm. tube and when made in shorter tubes are calculated to this basis for comparison. The "blank" filtrate solutions were always levorotatory and the result on slight or moderate proteolysis was to increase this levorotation; but with further digestive hydrolysis the levorotation was diminished. The results as shown in Table X are always averages of at least 3 or 4 readings.

The optical method shares with the titration and conductivity methods the advantage of rapidity, the relative convenience of these three methods depending upon the nature of the investigation and the equipment and arrangement of the laboratory. It also affords a delicate means of detecting the action of very small amounts of proteolytic enzyme; but the fact that the change in rotation does not proceed progressively with the amount of enzyme or the time during which a given amount of enzyme

<sup>1</sup> Initial conductivity, (1)  $6.56 \times 10^{-4}$ ; (2)  $6.56 \times 10^{-4}$ .

<sup>2</sup> "Abwehrfermente," 4th Ed., pp. 327-362.

<sup>3</sup> For the opportunity of using this instrument, which belongs to the Harriman Research Laboratory, we are indebted to Professor J. M. Nelson.

acts must necessarily interfere seriously with the use of this method for quantitative comparisons.

TABLE X.—CHANGE IN OPTICAL ROTATION OF FILTRATE RESULTING FROM ACTION OF DIFFERENT AMOUNTS OF COMMERCIAL ENZYMES UPON CASEIN SOLUTIONS AT 40°.

Mg. of commercial enzyme.	Half-hour digestions.		20-hour digestions.		
	Pepsin I.	Trypsin I.	Pepsin I.	Trypsin I.	Trypsin II.
	Change in terms of angular degrees in 220 mm. tube.				
0.001	0.00	0.00	0.00	0.00	....
0.002	0.00	0.00	—0.01	—0.03	—0.01
0.01	0.00	0.00	—0.07	—0.12	—0.07
0.05	0.00	0.00	—0.31	—0.56	—0.24
0.1	—0.02	—0.02	—0.52	—1.00	—0.55
0.5	—0.10	—0.10	—0.88	....	....
1	—0.24	—0.32	—1.18	—1.33	—1.29
2	—0.39	—0.60	—1.31	—1.30	—1.21
5	—0.66	—1.09	—1.42	—1.09	—1.02
25	—1.15	—1.26	—1.45	....	....
50	....	....	—1.34	....	....
100	....	—1.15	—1.33	....	....

### The Biuret Reaction.

The biuret test was applied to the filtrates obtained from the peptic and tryptic digestions of casein and the colors obtained were found to pass gradually from a faint violet to a rose-red according to the extent of the digestion, showing that the test may serve for rough comparisons of proteolytic power within the range covered by these color changes.

Five cc. portions of the filtrates were placed in small porcelain dishes and to each portion one cc. of a nearly saturated solution of sodium hydroxide, and 0.15 cc. (three drops) of a 1% solution of copper sulfate were added. The solutions were stirred and allowed to stand at least fifteen minutes in order to obtain a full development of color.

The readings are expressed as nearly as possible according to the Milton Bradley Standard Color Charts, as given by Mulliken in his *Identification of Pure Organic Compounds*. In the cases of the strongest digestions, the color is better described as rose-red, than as any shade on the color charts.

The results of these tests are shown in Table XI.

By comparison of these data with those given in previous tables, it will be seen that the application of the biuret reaction, while superior to the Mett method, is a less delicate means of detecting proteolysis than most of the quantitative measurements already described and is capable of showing differences only in a much narrower range of enzyme concentrations. For the purposes of our investigations the method did not seem sufficiently promising to warrant further study.

TABLE XI.—COLORS OBTAINED ON APPLYING BIURET REACTIONS TO FILTRATES FROM DIGESTIONS OF CASEIN WITH DIFFERENT AMOUNTS OF COMMERCIAL ENZYMES.

Mg. of commercial enzyme.	Half-hour digestions. Trypsin I. Color reading.	20-hour digestions.	
		Trypsin I. Color reading.	Pepsin I. Color reading.
0.000	Violet <sup>1</sup>	Violet <sup>1</sup>	Violet <sup>1</sup>
0.002	Violet <sup>1</sup>	Red-violet <sup>1</sup>	Violet <sup>1</sup>
0.01	Violet <sup>1</sup>	Red-violet <sup>1</sup>	Red-violet <sup>1</sup>
0.05	Violet <sup>1</sup>	Violet-red <sup>1</sup>	Red-violet <sup>1</sup>
0.1	Violet <sup>1</sup>	Red <sup>1</sup>	Violet-red <sup>1</sup>
1	Red-violet <sup>1</sup>	Rose-red	Violet-red <sup>1</sup>
2	Violet-red <sup>1</sup>	Rose-red	Red <sup>1</sup>
5	Red <sup>1</sup>	Rose-red	Rose-red
25	Rose-red	Rose-red	Rose-red
50	Rose-red	Rose-red	Rose-red
100	Rose-red	Rose-red	Rose-red

### The Triketohydrindene Hydrate (Ninhydrin) Reaction.

The filtrates from several of the experiments with casein substrate above described have been subjected to the ninhydrin reaction of Abderhalden and to Herzfeld's modification of this test. As this part of our work was done before the results of the investigations of Harding and MacLean<sup>2</sup> became available we did not have the opportunity to include their colorimetric method based on this reaction in our comparison; but from the striking agreement of their results with those which they obtained by the Van Slyke method it would seem that these methods may be regarded as giving practically identical information in the study of proteolysis induced by pancreatic enzymes.

In our experiments the ninhydrin tests were performed as follows: 5 cc. portions of the filtrates to be tested were dialyzed against 15 cc. of water for 16 hours at 37°, through the specially prepared "Abderhalden" parchment thimbles (No. 579A) of Schleicher and Schüll; the dialysates were then neutralized with sodium hydroxide and 10 cc. portions tested with 0.2 cc. of a 1% solution of ninhydrin: (1) According to Abderhalden, by adding the reagent to the aqueous dialysate and boiling for one minute; (2) according to Herzfeld,<sup>3</sup> by evaporating the dialysate and reagent to dryness and taking up the residue with 10 cc. of absolute alcohol.

Typical results are shown in Table XII.

The Herzfeld modification is plainly much more delicate than the test as described by Abderhalden—perhaps too delicate for the clinical purpose which the latter chiefly emphasizes. Thus Abderhalden<sup>4</sup> says:

"Schwierigkeiten machen einzig und allein rötliche und braungelbe Farbtöne. Sie haben nichts mit der eigentlichen Ninhydrinreaktion zu tun."

<sup>1</sup> In these cases the color was of only slight intensity approximating the "Tint 2" of the Standard Color Chart.

<sup>2</sup> *J. Biol. Chem.*, 20, 217 (1915); 24, 503 (1916).

<sup>3</sup> *Biochem. Z.*, 59, 249 (1914).

<sup>4</sup> "Abwehrfermente," 4th Ed., page 275.

TABLE XII.—COLORS OBTAINED ON APPLYING NINHYDRIN REACTION TO FILTRATES OBTAINED FROM DIGESTIONS OF CASEIN WITH DIFFERENT AMOUNTS OF COMMERCIAL ENZYMES.

Weight of commercial enzyme. Mg.	Half-hour digestions			20-hour digestions.		
	Trypsin I.			Trypsin I.		
	Color reading of:			Color reading of:		
	Water soln. (Abderhalden).	Alcohol soln. (Herzfeld).		Water soln. (Abderhalden).	Alcohol soln. (Herzfeld).	
0.000	Yellow <sup>1</sup>	Yellow <sup>1</sup>		Yellow <sup>1</sup>	Yellow <sup>1</sup>	
0.002	Yellow <sup>1</sup>	Yellow <sup>1</sup>		Yellow <sup>1</sup>	Yellow <sup>1</sup>	
0.01	Yellow <sup>1</sup>	Yellow <sup>1</sup>		Yellow <sup>1</sup>	Orange <sup>1</sup>	
0.05	Yellow <sup>1</sup>	Orange-yellow <sup>1</sup>		Yellow <sup>1</sup>	Orange-red <sup>1</sup>	
0.1	Yellow <sup>1</sup>	Red <sup>1</sup>		Orange <sup>1</sup>	Violet-red to Red-violet <sup>3</sup>	
1.0	Yellow <sup>1</sup>	Violet-red to Red-violet <sup>1</sup>		Violet to Red-violet <sup>3</sup>	Red-violet <sup>3</sup>	
2.0	Yellow <sup>1</sup>	Violet-red to Red-violet <sup>3</sup>		Violet to Red-violet <sup>3</sup>	Red-violet <sup>3</sup>	
4.0-5.0	Orange-yellow <sup>1</sup>	Violet-red <sup>3</sup>		Violet to Red-violet <sup>3</sup>	Red-violet <sup>3</sup>	
25.0	Orange-red <sup>1</sup>	Red-violet <sup>4</sup>		Violet-red to Red-violet <sup>3</sup>	Red-violet <sup>3</sup>	
50.0	Red-violet <sup>3</sup>	Red-violet <sup>4</sup>		Violet-red to Red-violet <sup>3</sup>	Red-violet <sup>3</sup>	
100.0	Red-violet <sup>3</sup>	Red-violet <sup>5</sup>		Violet-red to Red-violet <sup>3</sup>	Red-violet <sup>3</sup>	
			Tests negative (colorless to pale yellow)			
				Water soln. (Abderhalden).	Alcohol soln. (Herzfeld).	
				Yellow-orange <sup>1</sup>	Yellow-orange <sup>1</sup>	
				Orange <sup>1</sup>	Orange <sup>1</sup>	
				Red-orange <sup>1</sup>	Red-orange <sup>1</sup>	
				Violet-red <sup>3</sup> to Violet-red <sup>4</sup>	Violet-red <sup>3</sup> to Violet-red <sup>4</sup>	
				Violet-red to Red-violet <sup>3</sup>	Violet-red to Red-violet <sup>3</sup>	
				Violet <sup>3</sup>	Violet <sup>4</sup>	
				Violet <sup>4</sup> to Red-violet <sup>3</sup>	Violet <sup>4</sup> to Red-violet <sup>3</sup>	
				Violet <sup>4</sup> to Red-violet <sup>3</sup>	Violet <sup>4</sup> to Red-violet <sup>3</sup>	
				Violet <sup>4</sup> to Red-violet <sup>3</sup>	Violet <sup>4</sup> to Red-violet <sup>3</sup>	

<sup>1</sup> These colors were pale, approximating "Tint 2" of the Standard Color Chart; <sup>2</sup> "Tint 1;" <sup>3</sup> "Normal Tone;" <sup>4</sup> "Shade 1;" <sup>5</sup> "Shade 2;" <sup>6</sup> "Broken Tone (Medium)."

However, this may be from a clinical point of view, our experiments show that the solutions which gave an orange color in aqueous solution, contained a substance capable of reacting with ninhydrin because they gave a violet color when Herzfeld's conditions were used to make the test more sensitive. For example, the digestion containing 0.1 mg. of Trypsin I gave the color Orange, Tint 2, when the test was carried out in aqueous solution, and a color between Violet-red and Red-violet, Normal Tones, in alcoholic solution. Many other examples could be cited to the same effect.

But even with the increased delicacy given by the Herzfeld modification the ninhydrin test is, in our hands, a less delicate, and certainly a much less definite, means of demonstrating slight proteolytic action than is the determination of total nitrogen of digestion products or of amino nitrogen by the method of Van Slyke.

### Summary.

Eight methods for the study of proteolytic action have been examined: The Mett method, the determination of total nitrogen of digestion products, the measurement of increase of amino nitrogen by the Van Slyke method, the titration of acidity of digestion products, the increase of electrical conductivity, the polariscopic method, and the biuret and ninhydrin reactions.

The results obtained in comparable experiments upon typical commercial pepsin and trypsin are so tabulated as to permit detailed comparisons of the delicacy, accuracy and applicability of these methods. (The comparisons thus made possible are too numerous to be concisely summarized.)

In general it may be said that the quantitative determination of the total nitrogen or the amino nitrogen of the digestion products (or both) appears to be more delicate as a means of detecting proteolysis than either the biuret or the ninhydrin reaction and more delicate, accurate, and generally applicable as a means for its measurement than any of the other quantitative methods here studied.

The results emphasize the importance, in quantitative comparisons, of so limiting the amount of enzyme preparation and the time of its action as to keep within the region in which the velocity of hydrolysis is directly proportional to the enzyme concentration (Fig. 4.).

We are greatly indebted to the Carnegie Institution of Washington for grants in aid of this investigation.

LABORATORY OF FOOD CHEMISTRY,  
COLUMBIA UNIVERSITY, NEW YORK, N. Y.

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### CORRECTION.

In the article by C. S. Hudson and J. K. Dale in the July number of THIS JOURNAL (p. 1434, line 3 from bottom), entitled "The Isomeric



Pentacetates of Glucosamine and of Chondrosamine," the melting point of  $\beta$ -pentacetyl glucosamine recorded as 118–189° should be 188–189°.

### NEW BOOK.

**A System of Physical Chemistry.** Vol. I. Kinetic Theory. Vol. II. Thermodynamics and Statistical Mechanics. By WILLIAM C. MCC. LEWIS, Professor of Physical Chemistry in the University of Liverpool. Text-Books of Physical Chemistry, edited by Sir William Ramsay. New York and London: Longmans, Green and Co., 1916. Pp. xiv + 523, vii + 522. Price \$2.50 each volume.

In the preface the author states that "this book is intended to be used as a general text-book of physical chemistry by those who already possess some knowledge of both physics and chemistry," and "suggests to the reader the advisability of first familiarizing himself with the broad outlines" of physical chemistry. The "System" referred to in the title "consists in regarding all physico-chemical phenomena as being capable of separation into two classes: first, phenomena exhibited by material systems when *in* a state of equilibrium; and secondly, phenomena exhibited by material systems which have *not* reached a state of equilibrium." The book is divided "into three parts, in which the phenomena exhibited by systems in equilibrium and not in equilibrium are treated, first, from the 'classical' kinetic standpoint only (Vol. I); then independently from the thermodynamics; and finally from the standpoint of thermodynamics and the new or 'modified' principles of statistical mechanics (Vol. II)." This division into parts is not an essential feature of the System and is "introduced for the purpose of making the book as readable as possible from the students' point of view."

On account of the novel arrangement of the material the principal subjects considered are listed below:

Volume I, Part I. Chapters I and II, kinetic theory, evidence for the real existence of molecules (Perrin's work is discussed in detail), electron theory of matter, transmutation of the elements (radioactivity), continuity of the liquid and gaseous states, molecular association; Chapters III to VI, chemical equilibrium in homogeneous systems, law of mass action, gaseous systems, liquid mixtures, osmotic pressure, theory of electrolytic dissociation, solid solutions; Chapters VII and VIII, chemical equilibrium in heterogeneous systems, first in the absence of effects due to capillarity, radiation, etc., and second as modified by capillary and electro-capillary effects (colloidal solutions); Chapter IX, homogeneous systems not in equilibrium, diffusion, reaction velocity, catalysis; Chapter X, heterogeneous systems not in equilibrium, reaction velocity, catalysis.

Volume II, Part II. Chapters I and II, principles of thermodynamics; Chapter III, continuity of the liquid and gaseous states; Chapter IV, thermodynamic criteria of equilibrium; Chapters V to VIII, chemical

equilibrium in homogeneous systems, law of mass action, gaseous systems, dilute solutions, osmotic pressure, electrochemistry of dilute solutions, osmotic pressure of concentrated solutions; Chapters IX and X, parallel to VII and VIII above, phase rule, adsorption; Chapters XI and XII, parallel with IX and X above, affinity and its measurement, Nernst Heat Theorem.

Volume II, Part III. Chapter I, photochemistry; Chapter II, applications of the Quantum Theory.

Physical chemists will be especially interested in the excellent discussions of important recent investigations, such as the work on molecular reality, electron theory of matter, radioactive transformations, colloids, Nernst heat theorem, photochemistry, quantum theory and the calculation of the specific heats of solids. The date on the title page is 1916 but only a few brief references to work done since 1912 are given. The work on X-ray spectra and atomic numbers is entirely omitted.

An unusual and commendable feature of this book is the introduction of direct quotations from a number of original papers. The author has made it a point to present the principles of experimental methods and to give experimental results in some detail. These features, together with the large number of references to original papers and the excellence of the subject and author indexes for each volume make the book a valuable reference book for all chemists.

WILLIAM C. BRAY.

THE JOURNAL  
OF THE  
American Chemical Society

with which has been incorporated the

American Chemical Journal  
(Founded by Ira Remsen)

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ANNUAL REPORT OF THE INTERNATIONAL COMMITTEE ON  
ATOMIC WEIGHTS, 1917.

The following new determinations of Atomic Weights have been published since the issue of the last Annual Report:

**Hydrogen.**—Burt and Edgar<sup>1</sup> conclude from a long series of experiments that the ratio of the combining volumes of hydrogen and oxygen is represented with a high degree of probability by the figure 2.00288 at 0° and 760 mm. pressure. Assuming Morley's values for the densities of hydrogen and oxygen, namely 0.089873 and 1.42900, respectively, the atomic weight of hydrogen is found to be 1.00772. This new value for H is very nearly the arithmetic mean of the independent values obtained by Morley and Noyes. It may be taken, therefore, that the true value for H lies very close to 1.0077.

**Zinc.**—Baxter and Grose,<sup>2</sup> by the electrolysis of zinc bromide, find  $Zn = 65.388$ .

**Cadmium.**—Baxter, Grose and Hartmann,<sup>3</sup> by the electrolysis of cadmium bromide, find  $Cd = 112.407$ . Similar analyses of the chloride gave  $Cd = 112.413$ . Oechsner de Coninck and Gérard,<sup>4</sup> by reducing cadmium carbonate to metal, found  $Cd = 112.32$ .

<sup>1</sup> *Phil. Trans.*, 216, 393 (1916).

<sup>2</sup> *THIS JOURNAL*, 38, 868 (1916).

<sup>3</sup> *Ibid.*, 38, 857 (1916).

<sup>4</sup> *Compt. rend.*, 161, 676 (1915).

**Lead.**—Hönigschmid and Horovitz,<sup>1</sup> by analyses of the chloride, found for common lead the value  $Pb = 207.180$ . Similar analyses of radioactive lead chloride from various sources gave atomic weight values ranging from 206.050 to 206.084.

## INTERNATIONAL ATOMIC WEIGHTS, 1917.

	Symbol.	Atomic weight.		Symbol.	Atomic weight.
Aluminum.....	Al	27.1	Molybdenum.....	Mo	96.0
Antimony.....	Sb	120.2	Neodymium.....	Nd	144.3
Argon.....	A	39.88	Neon.....	Ne	20.2
Arsenic.....	As	74.96	Nickel.....	Ni	58.68
Barium.....	Ba	137.37	Niton (radium emanation) Nt		222.4
Bismuth.....	Bi	208.0	Nitrogen.....	N	14.01
Boron.....	B	11.0	Osmium.....	Os	190.9
Bromine.....	Br	79.92	Oxygen.....	O	16.00
Cadmium.....	Cd	112.40	Palladium.....	Pd	106.7
Caesium.....	Cs	132.81	Phosphorus.....	P	31.04
Calcium.....	Ca	40.07	Platinum.....	Pt	195.2
Carbon.....	C	12.005	Potassium.....	K	39.10
Cerium.....	Ce	140.25	Praseodymium.....	Pr	140.9
Chlorine.....	Cl	35.46	Radium.....	Ra	226.0
Chromium.....	Cr	52.0	Rhodium.....	Rh	102.9
Cobalt.....	Co	58.97	Rubidium.....	Rb	85.45
Columbium.....	Cb	93.1	Ruthenium.....	Ru	101.7
Copper.....	Cu	63.57	Samarium.....	Sa	150.4
Dysprosium.....	Dy	162.5	Scandium.....	Sc	44.1
Erbium.....	Er	167.7	Selenium.....	Se	79.2
Europium.....	Eu	152.0	Silicon.....	Si	28.3
Fluorine.....	F	19.0	Silver.....	Ag	107.88
Gadolinium.....	Gd	157.3	Sodium.....	Na	23.00
Gallium.....	Ga	69.9	Strontium.....	Sr	87.63
Germanium.....	Ge	72.5	Sulfur.....	S	32.06
Glucinum.....	Gl	9.1	Tantalum.....	Ta	181.5
Gold.....	Au	197.2	Tellurium.....	Te	127.5
Helium.....	He	4.00	Terbium.....	Tb	159.2
Holmium.....	Ho	163.5	Thallium.....	Tl	204.0
Hydrogen.....	H	1.008	Thorium.....	Th	232.4
Indium.....	In	114.8	Thulium.....	Tm	168.5
Iodine.....	I	126.92	Tin.....	Sn	118.7
Iridium.....	Ir	193.1	Titanium.....	Ti	48.1
Iron.....	Fe	55.84	Tungsten.....	W	184.0
Krypton.....	Kr	82.92	Uranium.....	U	238.2
Lanthanum.....	La	139.0	Vanadium.....	V	51.0
Lead.....	Pb	207.20	Xenon.....	Xe	130.2
Lithium.....	Li	6.94	Ytterbium (Neoytterbium) Yb		173.5
Lutecium.....	Lu	175.0	Yttrium.....	Yt	88.7
Magnesium.....	Mg	24.32	Zinc.....	Zn	65.37
Manganese.....	Mn	54.93	Zirconium.....	Zr	90.6
Mercury.....	Hg	200.6			

<sup>1</sup> *Monatsh.*, 46, 355 (1915).

**Bismuth.**—Oeschner de Coninck and Gérard,<sup>1</sup> by reduction of bismuth chloride to metal, found Bi = 208.50.

**Molybdenum.**—Müller,<sup>2</sup> by oxidation of the metal, found Mo = 96.035.

**Neodymium.**—Baxter, Whitcomb, Stewart, and Chapin,<sup>3</sup> by analyses of the chloride, find Nd = 144.27.

**Columbium.**—Smith and Van Haagen,<sup>4</sup> from the ratio between sodium columbate ( $\text{NaCbO}_3$ ) and sodium chloride, find Cb = 93.13. The value 93.1 might be adopted in the table.

**Argon.**—Schultze<sup>5</sup> has redetermined the density of argon. The corresponding atomic weight is A = 39.945.

Signed, F. W. CLARKE,  
T. E. THORPE,  
G. URBAIN.

NOTE.—Because of the European war the Committee has had much difficulty in the way of correspondence. The German member, Professor Ostwald, has not been heard from in connection with this report. Possibly the censorship of letters, either in Germany or *en route*, has led to a miscarriage.

F. W. CLARKE, *Chairman*.

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[CONTRIBUTION FROM RESEARCH LABORATORY OF THE GENERAL ELECTRIC COMPANY, SCHENECTADY, N. Y.]

## THE CONSTITUTION AND FUNDAMENTAL PROPERTIES OF SOLIDS AND LIQUIDS.

### PART I. SOLIDS.

BY IRVING LANGMUIR.

Received September 5, 1916.

The importance of the work of W. H. Bragg and W. L. Bragg in its bearing on chemistry has not, as yet, been generally recognized. In hearing two of W. H. Bragg's lectures in this country a few years ago, the writer was impressed with the very great significance of this work in the field of chemistry. The structure of crystals as found by the Braggs leads to new and more definite conceptions as to the nature of chemical forces.

The writer has constantly endeavored to apply this new conception in his work on heterogeneous reactions and particularly in connection with a study of the phenomena of adsorption and surface tension. In this way he has gradually been led to form more or less definite theories of the mechanism of evaporation, condensation, liquefaction, adsorption, and capillary phenomena. According to this theory, both solids and liquids

<sup>1</sup> *Compt. rend.*, 162, 252 (1916).

<sup>2</sup> THIS JOURNAL, 37, 2046 (1915).

<sup>3</sup> *Ibid.*, 38, 302 (1916).

<sup>4</sup> *Ibid.*, 38, 1783 (1916).

<sup>5</sup> *Ann. Physik*, [iv] 48, 269 (1915).

consist of atoms held together entirely by *chemical forces*. The conception of the molecule thus almost entirely loses its significance except in the case of gases. In fact, we may well look upon any solid or liquid body as constituting a single large molecule. Any change of phase, such as the melting of a solid, is thus a typical chemical reaction. The mobility of liquids, according to this viewpoint, is due to a kind of tautomerism.

The present paper is merely an outline of this theory. The more detailed description of the experimental work upon which it is largely based, will be reserved for future papers.

### STRUCTURE OF CRYSTALS.

The idea that a crystal should constitute an effective diffraction grating for X-rays originated with Laue,<sup>1</sup> who also saw that by means of such a grating not only could the wave length of the X-rays be determined, but also a powerful method for studying the structure of crystals was made available. The detailed theory developed by Laue proved incorrect in certain important respects. W. L. Bragg<sup>2</sup> called attention to these errors and gave a theory by which the true structure could be determined from the diffraction pattern. Since then the method has been greatly simplified, so that at present it is usually a matter of no great difficulty to find the exact arrangement of the atoms in a crystal. In this way the structures of some 30 or more kinds of crystals have been determined.

The alkali halides NaCl, KCl, KBr, and KI all have a similar structure in which the *atoms* are arranged according to a simple cubic lattice. Thus, in the case of sodium chloride crystals, sodium and chlorine atoms alternate along three sets of lines at right angles to each other. Each sodium atom is surrounded by six equidistant chlorine atoms arranged around it, as the corners of an octahedron are arranged around its center. Similarly, each chlorine atom is surrounded by six equidistant sodium atoms.

Up to this time it had been taken for granted that crystals were built up of molecules. But from this work of the Braggs it is clear that in crystals of this type the identity of the molecules is wholly lost, except in so far as we may look upon the whole crystal as composing a single molecule. From the arrangement of the atoms we must conclude that the forces holding the crystal together (cohesion) are forces which exist directly between sodium and chlorine atoms. Every chemist looks upon such forces as chemical in nature.<sup>3</sup>

<sup>1</sup> *Sitzb. d. Bayer. Akad. d. Wiss.*, June, 1912.

<sup>2</sup> *Proc. Camb. Phil. Soc.*, 17, 43 (1912). The subsequent papers of W. H. and W. L. Bragg were published in 1913 and 1914 in the *Proc. Camb. Phil. Soc.*, the *Proc. Roy. Soc.*, and the *Phil. Mag.* All of these papers were translated into German and were published together in one volume of the *Z. anorg. Chem.*, 90 (1914).

<sup>3</sup> Of course all chemical forces are probably of electromagnetic origin, but for this reason we do not need to call the forces in crystals by the vague term "physical forces" (and thus distinguish them from chemical force).

But the significance of this structure for the chemist extends further. Sodium is invariably regarded as a monovalent element, yet in the sodium chloride crystals we see a structure which in no wise suggests the monovalent character of the atom. The sodium atom is held by chemical forces to six chlorine atoms. If we retain the conception of valency in such a case, we must clearly admit that the valency of the sodium is divided equally between the six chlorine atoms.

If a sodium chloride crystal evaporates at high temperature, the atoms leave the surface in pairs in the form of sodium chloride molecules. These molecules are formed in the process of evaporation, since they do not exist as such in the crystal. The process of evaporation is thus a chemical process.

In the diamond, each carbon atom is surrounded by four others equidistant from it. These are arranged around the central one in the same way as the four corners of a regular tetrahedron are arranged around its center. In this case the tetravalent character of the carbon atom manifests itself clearly. When a model of a diamond crystal is examined, it is seen that the atoms appear to be arranged in rings of six, corresponding to the benzene ring. The remarkable strength of the carbon chain and especially the stability of the benzene ring, so familiar to chemists, is thus seen to be the cause of the hardness, the high melting point and the low vapor pressure of the diamond.

It is interesting to note that the structure of zinc blend,  $\text{ZnS}$ , is very similar to that of the diamond, the zinc and sulfur being alternately substituted for adjacent carbon atoms. Thus each zinc atom is surrounded by four symmetrically placed sulfur atoms, while each sulfur atom is surrounded by four zinc atoms. The valency is thus again divided.

With fluorite,  $\text{CaF}_2$ , each fluorine atom is surrounded by four symmetrically placed calcium atoms, while each calcium atom has eight fluorine atoms arranged around it like the eight corners of a cube about the center of the cube.

The structure of pyrites,  $\text{FeS}_2$ , is much more complicated. Each iron atom has four equidistant sulfur atoms around it, but there are other sulfur atoms at distances only slightly greater. Similarly, each sulfur atom has three equidistant iron atoms forming a triangle around it, but above and below the plane of this triangle there are other iron atoms whose distance is only slightly greater.

Hauerite,  $\text{MnS}_2$ , has a similar structure to that of pyrites.

In the case of calcite,  $\text{CaCO}_3$ , the carbon and oxygen atoms lie in planes perpendicular to the crystal axis. Three oxygen atoms are arranged in groups around each carbon atom, forming an equilateral triangle. The calcium atoms lie in planes just above and just below the carbon-oxygen planes. Each calcium atom has six equidistant oxygen atoms around it.

The distance between the calcium and the carbon atoms is considerably more than either the distance between oxygen and carbon, or between oxygen and calcium. Thus the crystal is evidently held together by forces acting between carbon and oxygen and between oxygen and calcium. The group  $\text{CO}_3$  appears as a unit, since each carbon atom is associated with three oxygen atoms while these are associated with only the one carbon atom. But each  $\text{CO}_3$  group is equidistant from six calcium atoms, so that it is impossible to pick out any one of these as forming a molecule with the  $\text{CO}_3$ . If we are to retain the idea of a molecule at all, we must consider that the entire crystal is a single molecule.

In dolomite,  $\text{CaMgCO}_3$ , the structure is exactly similar except that calcium and magnesium planes alternate. The structures of rhodochrosite,  $\text{MnCO}_3$ , siderite,  $\text{FeCO}_3$ , and sodium nitrate,  $\text{NaNO}_3$ , are like that of calcite. This last case is of special interest to the chemist, since a monovalent atom replaces a divalent, and a pentavalent (?) atom replaces a tetravalent one without causing a change in the arrangement of the atoms.

The crystals of magnetite afford an illustration of a structure in which different atoms of the same element have different functions. Two-thirds of the iron atoms occur in positions in which each is surrounded by four oxygen atoms (tetrahedral arrangement), while the other third of the iron atoms are each surrounded by six oxygen atoms. The iron atoms have thus a divalent and trivalent character, but each unit of valence is divided between two oxygen atoms. Spinel,  $\text{MgAl}_2\text{O}_4$ , has an exactly similar structure in which the Mg atoms take the place of the divalent iron atoms, while the Al atoms replace the trivalent iron atoms.

Crystals of metallic copper and metallic silver have been found to have their atoms arranged according to the face-centered cubic lattice. This arrangement is the same as the familiar one obtained when round shot are piled in layers as regularly and compactly as possible. In this structure each atom is equidistant from the twelve adjacent atoms.

The structures of crystals of rhombic sulfur and quartz have been partly worked out. In the sulfur crystals the atoms are found to be arranged in a lattice structure in groups of eight. The particular arrangement of the atoms within these groups is not yet known. To the chemist it is of significance that these groups of eight contain the same number of atoms as are found in molecules of sulfur vapor. Here, then, for the first time, the crystal has a structure in which the identity of the molecules (as found in the gas phase) is apparently not wholly lost.

In a recent article<sup>1</sup> L. Vegard shows that the structures of gold and lead crystals are the same as those of silver and copper. He also describes the structure of the zircon group of minerals represented by zircon,  $\text{ZrSiO}_4$ ,

<sup>1</sup> *Phil. Mag.*, 32, 65 (1916).



rutile,  $\text{TiO}_2$ , and cassiterite,  $\text{SnO}_2$ . The structure of zircon proves to be especially interesting, for it is found "that each of the Zr or Si atoms is associated with two oxygen atoms; thus the groups  $\text{SiO}_2$  and  $\text{ZrO}_2$  form a kind of 'molecular elements' of the lattice. This is not merely a way of regarding the geometrical arrangement of the atoms; but we have reason to believe that the groups  $\text{SiO}_2$  and  $\text{ZrO}_2$  form chemically saturated compounds" within the crystal.

Two facts stand out clearly as a result of the consideration of these crystal structures. In the first place, it is evident that crystals are built up of atoms in such a way that each atom is chemically combined to all the adjacent atoms, while these in turn are combined to those beyond.

Secondly, we see that the arrangement of the atoms in general does not follow the usual rules of valency, but that each atom is combined with a much larger number of atoms than corresponds to its normal valence.

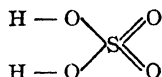
In the past it has been customary to consider that solids and liquids are held together by the "forces of cohesion" and to call these "physical forces" as distinguished from chemical forces. Often these distinctions are known to be rather vague, but in the more recent years, with growing confidence in the atomic theory, we have been accustomed to consider that chemical phenomena are those involving an alteration of the structure of molecules, while physical phenomena are those in which only the molecule as a whole is concerned. This distinction throws the whole difficulty back on to the definition of the molecule. In gases there is usually no uncertainty as to the size of the molecules, but in liquids and solids no really satisfactory methods have been found for determining molecular weights. As long as we cannot definitely determine the molecular weights, it thus remains impossible to distinguish sharply between chemical and physical phenomena. Nevertheless, much discussion has arisen of late years over such questions as whether adsorption and surface tension are chemical or physical phenomena. The overwhelming consensus of opinion seems to be that these are both physical phenomena.

In the following pages the writer hopes to show that there is no present justification for this distinction between chemical and physical forces. Cohesion, adsorption and surface tension are all manifestations of forces similar in their nature to those acting between the atoms of solid bodies. It is therefore advantageous to look upon these forces as direct results of chemical affinity. In this way it becomes possible to correlate these so-called physical phenomena with the known chemical characteristics of the atoms and groups of atoms forming the bodies.

**Theories of Chemical Constitution.**—The fact that each atom in a crystal is usually combined with a larger number of adjacent atoms than corresponds to its valence, is not in conflict with recent theories of the constitution of chemical substances.

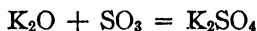
A. Werner<sup>1</sup> has made a very extensive study of complex inorganic compounds, and as a result has established a theory of residual or secondary valence.

In accordance with the ordinary theory of valency which has proved so invaluable in organic chemistry, it has been customary to assign structural formulas of similar type to inorganic compounds. Thus the graphic formula for sulfuric acid is often written



Whereas among organic compounds the structural formulas can be determined with certainty and undoubtedly correspond to the actual arrangement of the atoms in the molecules, no such certainty is ever found in the case of complex inorganic compounds. As a result, such formulas have served no useful purpose in the development of inorganic chemistry. In fact, Werner claims that the common acceptance of such conceptions was responsible for the fact that our knowledge of the constitution of inorganic compounds failed to progress for so many years.

Werner<sup>2</sup> then shows clearly that such formulas are untenable. In the first place, the formula would lead to a sharp distinction between the combination of oxides and halides, whereas such a distinction does not actually exist. A proper theory should show a close relationship between such reactions as



and



The same kind of relations exist with complex cyanides, nitrites, etc., and these cannot be accounted for by the ordinary theory of valency.

Secondly, the ordinary theory would indicate that oxides such as  $\text{OsO}_4$ ,  $\text{RuO}_4$ , etc., should easily form acids by combination with water. Actually, it is found that the number of molecules of water which can be taken up by an oxide does not bear any definite relation to the number of doubly bound oxygen atoms.

Several other good reasons are given against the ordinary graphic formula for such compounds.

Werner then proceeds to show that the ordinary conception of (primary) valence applies (except in organic compounds) practically only to compounds of the first order; that is, to simple compounds containing not more than two elements, such as  $\text{H}_2\text{O}$ ,  $\text{NaCl}$ ,  $\text{SO}_3$ , etc.

Compounds of higher order are formed when compounds of the first

<sup>1</sup> *Neuere Anschauungen auf dem Gebiete der Anorganischen Chemie*, Braunschweig (1905).

<sup>2</sup> *Loc. cit.*, p. 42.

order combine together. Thus Werner draws no sharp distinction between the combination of  $P_2O_5$  and  $Na_2O$  to form  $Na_3PO_4$ , and such a process as the taking up of "water crystallization" by a salt such as  $BaCl_2$  to form  $BaCl_2 \cdot 2H_2O$ .

When two elements combine to form a compound of the first order, their primary valences become saturated. But there is still a field of force around the molecule which enables it to combine with other molecules to form compounds having almost any degree of stability. The molecules are then said to be held together by residual or secondary valence.

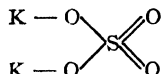
Werner gives the following definitions of primary and residual valency:

(a) "Primary valence serves to unite those simple or complex radicals which can exist as separate ions or whose chemical combining power is equivalent to an ionizable radical."

(b) "Residual valence represents the affinity that binds together radicals which can neither act like nor be equivalent to separate univalent ions."

As illustrations of primary valence, he gives  $-Cl$ ,  $-Na$ ,  $-NO_2$ ,  $-CH_3$ , and for residual valence :  $OH_2$ , :  $NH_3$ , :  $ClK$ , and :  $CrCl_3$ .

R. Abegg<sup>1</sup> advanced a somewhat similar theory of the constitution of inorganic compounds. He looks upon salts of oxygen acids, for example, as consisting of basic and acid oxides held together by secondary valence. He considers Berzelius' idea of the structure of such compounds ( $K_2O \cdot SO_3$ , for instance) to be much preferable to the structural or graphic formula



and gives many good reasons to support his contention.

Stark<sup>2</sup> has developed a theory of the mechanism of chemical valency based on the electron theory. This electroatomic theory gives symbolically a very satisfactory picture of the different types of valence. According to Stark, portions of the surfaces of atoms contain an excess of positive electricity. In the neutral atom one or more electrons are held close to the surface of the atom by this positive charge. Compounds are formed when the lines of force from one of these "valence electrons" reach out and end on the positive areas of other atoms. In the case of strongly polar compounds, an electron is almost wholly drawn over to the atom which it holds in combination. Primary valences are due to a pair of valence

<sup>1</sup> *Z. anorg. Chem.*, **39**, 330 (1904); **50**, 309 (1906), and *Z. physik. Chem.*, **69**, 1 (1909).

<sup>2</sup> *Jahr. d. Radioakt. und Elek.*, **5**, 125 (1908); *Prinzipien der Atomdynamik*, Vol. 3; "Die Elektrizität im chemischen Atom," Leipzig, 1915. A short description of Stark's theory of valence was given by Misses Hahn and Holmes in *THIS JOURNAL*, **37**, 2611 (1915). This article is essentially an abstract of Paul Ruggli's book, "Die Valenzhypothese von J. Stark vom Chemischen Standpunkt," Stuttgart, 1912.

electrons whose field binds two atoms together. The stray electric field in the space around the resultant molecule is the cause of the residual valence. This theory accounts particularly well for the gradations between primary and secondary valence.

Thus when two atoms combine chemically, they are held together by certain electrons which are common to both atoms. Bohr's model of the hydrogen molecule assumes a similar function of the electrons. According to Bohr's theory, a hydrogen atom consists of a positive nucleus around which (at a distance of  $0.55 \times 10^{-8}$  cm.) an electron revolves with very high speed. The hydrogen molecule, on the other hand, consists of two hydrogen nuclei (at a distance apart of  $0.60 \times 10^{-8}$  cm.) and two electrons which revolve in an orbit in a plane perpendicular to the line joining the nuclei. The radius of the orbit of the electrons is  $0.52 \times 10^{-8}$  cm. In the hydrogen atom the electron forms part of the atom. When two atoms combine the two nuclei share the two electrons equally. If the two atoms separate again, there is an even chance that they will have exchanged electrons. The two electrons held in common by the two nuclei hold the molecule together and are thus equivalent to the bond by which we ordinarily imagine two univalent atoms to be joined. This model of the univalent bond is remarkably similar to that proposed by Stark.

J. J. Thomson<sup>1</sup> has also developed a theory of the mechanism of chemical affinity. On the whole, his theory is very much like that of Stark. Thomson considers that the electrons near the surface of an atom, together with the positive charge in the core of the atom, constitute one or more electric doublets which exert forces not only on free electrons or ions in their neighborhood, but also on other electric doublets. The force of attraction between such doublets varies much more rapidly with the distance than the inverse square. Thomson uses the dielectric constant of the substance in the gaseous condition as a measure of the moment of the electric doublets. In this way he concludes that there has been an actual transfer of an electron from one atom to another in such compounds as  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{SO}_2$ ,  $\text{HCl}$ ,  $\text{CH}_3\text{OH}$ ,  $\text{C}_2\text{H}_5\text{OH}$  and  $\text{CH}_3\text{Cl}$ , even when these are in the gaseous condition. This "intra-molecular ionization" greatly increases the moment of the doublet by increasing the distance between the charges. In other types of compounds, however, Thomson believes that the atoms are electrically neutral and are held together by one or more doublets on each atom. As compounds of this type he cites  $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{Cl}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{CS}_2$ ,  $\text{CCl}_4$ ,  $\text{C}_6\text{H}_6$ ,  $\text{CH}_4$ ,  $\text{N}_2\text{O}$ .

It should be noted that Stark's theory recognizes both these types and indicates how there may be all possible gradations between these extremes.

<sup>1</sup> *Phil. Mag.*, 27, 757 (1914).

Thomson also believes that the more complex compounds are "molecular compounds" in which simple molecules are held together by the stray field around the molecules. In the first paragraph of his paper he says: "These forces will be exerted by the atom not merely on the atoms which are associated with it in the molecule of a chemical compound, but also on the atoms in other molecules, giving rise to forces between the molecules and producing thereby the intrinsic pressure and surface tension of liquids, latent heat of evaporation, cohesion of solids and liquids, the rigidity of solids and so on. These physical phenomena are the effects of forces between different molecules, whereas chemical affinity and chemical phenomena in general are the effects of forces having the same origin, but acting between the atoms of the same molecule."

We shall see that this division of solids and liquids into molecules is very arbitrary and that the same kind of chemical relationships exist between these forces, which Thomson calls physical, as exist among the forces which cause the formation of molecular compounds.

In regard to saturated valence, Thomson considers that two electrons are involved in holding two univalent uncharged atoms together. In this respect his theory is like those of Stark and Bohr. He points out, however (as Stark has also done), that by this theory three univalent atoms may be held together in the form of a ring, one electron being located between each pair of adjacent atoms. He says: "The difference between the theory we are considering and the accepted theory of valency may be expressed by saying that not only is every possible valency compound on the old theory a valency compound on this theory, but every compound which would be a valency one on the old theory if the valency of every element was doubled, would be a valency compound on the new, with the atoms retaining their original valency. This only applies to the compounds when the atoms are uncharged; when the atoms are charged the valency conditions are the same as on the old theory."

This theory would seem to fit in badly with the facts of organic chemistry, for we find no evidence of organic compounds in which carbon acts as if it had a valency of eight or hydrogen a valency of two. But in the formation of crystals this theory suggests an explanation of the divided valence observed in crystals of the spinel group. For instance, it was found in magnetite that the *divalent* iron atoms were surrounded by *four* symmetrically placed oxygen atoms, while the *trivalent* iron atoms were surrounded by *six* oxygens.

An extremely important theory of the "Atom and Molecule" is that recently described by G. N. Lewis.<sup>1</sup> Substances are classified into two general groups: polar and nonpolar. The polar type, represented by  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{NaCl}$ , etc., is characterized by reactivity, high dielectric constant,

<sup>1</sup> THIS JOURNAL, 38, 762 (1916).

tendency to form molecular complexes, etc. Tautomerism is a "predominant trait of most inorganic substances (polar type), which behave as if a great variety of forms were existing together in extremely mobile equilibrium."

For this reason Lewis<sup>1</sup> believes that the constitution of the more complex inorganic compounds cannot be represented by any single structural formula.

We shall see that these ideas on tautomerism will prove of value in connection with a study of the constitution of liquids.

**Crystal Structure from the View Point of Chemical Theory.**—The work that has been done so far on crystal structure testifies to the general applicability of such theories of chemical constitution as that of Werner.

Except in the case of diamond crystals, no structural formula can be written consistent with our ordinary ideas of (primary) valence, which adequately represents the constitution of the crystal. We see, however, that the arrangement of the atoms in crystals is just what we should expect if the forces binding the atoms together are similar to those forces which, by Werner's theory must hold together the *molecules* in molecular compounds (compounds of higher orders).

Werner's theory, however, needs to be modified in some respects, to fit in with the new work. According to Werner, compounds of the first order are held together by primary valence, and only when these simple compounds form compounds of higher orders are the residual valences called into play. But when we consider the structure of the halide salts of the alkalis and the structure of such crystals as fluorite, we must conclude that even in the case of these first order compounds the ordinary rules of valence do not always apply.

It thus seems that secondary, or residual valence is active, not only in the higher order compounds, but that a valency of the secondary type may also characterize single atoms when these are combined with others in crystals.

It is evident that solid bodies could not be built up of atoms held together exclusively by primary valences except in the case of atoms having valences of four or more. Thus, when two monovalent atoms combine to form a gas molecule, they are held together by primary valence. If there were no residual valence, these molecules could not condense either as a solid or liquid. Divalent atoms could combine together in long chains, but these chains could not be linked together except by secondary valence. With trivalent atoms branching chains could be formed which could interlock so as to cover a plane surface, but except by secondary valence no atoms could be held outside of this plane. With tetravalent

<sup>1</sup> THIS JOURNAL, 35, 1448 (1913).

atoms, on the other hand, the atoms can be linked together by their primary valences, as in the diamond crystal, so as to fill a volume.

We thus see that primary valences cannot play an important part in crystal structure in the case of atoms with a valency of less than four. Most of the crystals containing tetravalent atoms which have been studied so far, have shown that the primary valences of the tetravalent atoms seem to exert their influence. This is shown not only in the case of the diamond, but in zircon, cassiterite and rutile, in which each atom of Zr, Si, Ti or Sn is clearly associated with two atoms of oxygen.

From these considerations it seems that in general there is a strong tendency for every atom to form compounds by means of its primary valence, but where the conditions are such that combination by primary valence is no longer possible, then secondary valence is called into play and may entirely supersede the primary valence.

Thus, when sodium atoms and chlorine atoms combine at high temperatures to form gaseous NaCl, the primary valence holds the atoms together. But when the pressure is raised or the temperature is lowered, the secondary valence is enabled to completely supersede the primary valence, since the primary valence cannot cause the combination of the molecules necessary to form a solid body.

With divalent and trivalent atoms a sort of divided valence like that suggested by J. J. Thomson, is apparently often manifest and is probably a sort of transition between primary and secondary valence. This is seen particularly in crystals of the spinel group, in which the divalent atoms have assumed a tetravalent character and the trivalent atoms a hexavalent character.

By this division of each of the valence units into two parts, the apparent valency is raised to four or more, so that the solid body can then be held together by this means. According to Stark and J. J. Thomson's theories, we should never expect the subdivision of a primary valence unit into more than two parts. Furthermore, we should not expect that a monovalent element would often exhibit this divided valence in solid bodies, because, even if its apparent valence was doubled by this means, it still would not be able to make use of this valence in forming a crystal.

The compounds whose crystal structures have been studied thus far, are all more or less of the polar type. It is not safe to conclude that the structures of nonpolar compounds will be similar to those already found.

For example, when an organic compound such as methane, is crystallized as a solid and is then converted again into a gas, it is certain, from chemical considerations, that none of the hydrogen atoms have been separated from the carbon atoms to which they were originally attached. The identity of the original molecules must, in a sense, have been preserved even when the methane was in the solid condition.

On the other hand, with crystals of the types studied so far, the substance could not be condensed from the gaseous condition and be re-evaporated again without most of the atoms having exchanged partners. Thus, when a crystal of sodium chloride evaporates, a sodium atom on the surface may escape with any one of the four adjacent chlorine atoms as a molecule of salt vapor. There is only a small chance that the particular chlorine atom with which it escapes will be the same one as that with which the sodium atom was combined before it formed part of the crystal.

From these considerations we are forced to conclude that in crystals of methane each carbon atom is surrounded by four hydrogen atoms held to it by primary valences. The crystal is then held together by residual valences. Since the methane is so thoroughly saturated chemically, these residual forces are very weak and, therefore, methane melts and boils at a very low temperature. But there is absolutely no reason for assuming that these residual forces are any less chemical in nature than those which cause the combination of  $K_2O$  and  $SO_3$  to form  $K_2SO_4$ . We certainly cannot limit chemistry to a study of only those substances whose atoms are held together by primary valence.

Determination of the crystal structure of organic compounds should prove of very great value in clearing up the true distinctions between primary and secondary valence. Unfortunately, the very low absorption of X-rays by the hydrogen makes it difficult to determine the positions of the atoms of this element by the present methods. This difficulty can be avoided by choosing such substances as  $C_2Cl_6$  and  $C_6Cl_6$ .

Similar considerations to those used with methane apply to such substances as  $H_2$ ,  $N_2$ ,  $O_2$ , etc., and nearly all typical organic substances. That the crystal structure, even with these substances, depends on the space arrangement of the atoms, is clear from the work of W. Wahl<sup>1</sup> on the crystal forms of the lower members of the aliphatic hydrocarbon series. He finds methane crystallizes in the isometric system, ethane in the hexagonal, propane apparently rhombic, trimethyl methane probably rhombic. Tetramethyl methane occurs in two modifications, one isometric and one tetragonal. Normal butane also has two forms, hexagonal and rhombic. Normal pentane is rhombic, while normal hexane, heptane and octane are monoclinic or triclinic.

The lower members of this series show a remarkable agreement between the chemical constitution and the crystal form. Thus the symmetry of the methane molecule requires a crystal of the isometric form, probably with an arrangement rather similar to that of the diamond. If we look upon the carbon atom as having its bonds arranged symmetrically after the pattern of the tetrahedron, then the ethane molecule would con-

<sup>1</sup> *Proc. Roy. Soc., (A)* **88**, 354 (1913).



sist of two carbon atoms each with three hydrogen atoms (in planes  $120^\circ$  apart) arranged around them. This leads naturally to the hexagonal form.

The definiteness of this dependence of the crystalline form upon the arrangement of the atoms indicates that even with these nonpolar compounds the forces holding the *molecules* together in the crystals are of the same nature as those holding the *atoms* together in the polar types of crystals.

Since the forces acting between the molecules in these crystals are then quite similar to those acting in the more complex inorganic compounds we would still be justified in regarding a crystal of methane as one large molecule. We thus have molecules within the molecule.

This leads us to consider whether it is not desirable to revise our conception of the molecule. There is an advantage in looking upon every crystal (and in fact every mass of liquid) as a single large molecule, in that this viewpoint brings out strongly the *chemical* nature of the forces holding the crystal together, and thus encourages us to apply to the study of these forces the knowledge already available from other fields of chemistry.

On the other hand there is a real need for a term to denote a group of atoms which can pass from the gas phase to the solid (or liquid) and back again without the exchange of any atoms. If, however, we should limit the word molecule (in liquids and solids) to this narrow definition, we would have to say that there are no molecules at all in the great majority of inorganic substances.

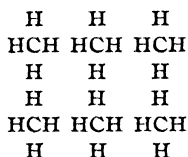
On the whole, it seems best to define a molecule as *a group of atoms held together by atomic forces*. We must then distinguish between various kinds of molecules.

The *gas molecule* may be defined in terms of Avogadro's Law, and is thus only sharply definable in so far as the gas follows the laws of ideal gases. We may define a *fixed molecule* as the largest aggregate of atoms which may pass from the gaseous phase to the solid (or liquid phase) and back again to the gaseous phase without exchange of atoms with other aggregates. With substances which are wholly nonpolar, such as the saturated hydrocarbons, this definition of fixed molecule is probably never ambiguous. But with molecules which are partly polar, as for example acetic acid, this definition may lack sharpness. Thus when  $\text{CH}_3\text{COOH}$  vapor dissolves in water (or condenses as a solid), it is probable that the replaceable hydrogen atom will be exchanged with that of the other  $\text{CH}_3\text{COO}$  groups. According to our definition of fixed molecule we must, therefore, consider that the *fixed molecules* in liquid or solid acetic acid consist of  $\text{CH}_3\text{COOH}$  groups. Cases will frequently arise, as for example in the alcohols, where the rate of exchange of the hydrogen atoms is so

slow as to be almost negligible, so that it will be impossible to limit sharply the extent of the fixed molecule. This difficulty, however, seems an inherent one, for it depends upon the fact that all possible degrees of tautomerism may actually exist in the large molecule forming the whole mass of the solid or liquid.

It will also be convenient to distinguish another type of molecule which we may call the *group molecule*. This may be defined as an aggregate of atoms which are interrelated in such a way (by position or mobility) that the atoms in the group may be distinguished from atoms outside the group. Thus in solid methane each hydrogen atom is associated with a particular carbon atom, while the carbon atom is associated with four hydrogen atoms. All other hydrogen atoms beside these four may be distinguished from these by their being combined with a different carbon atom.

If we represent a methane crystal diagrammatically as follows:



it is evident that we might also look upon the crystal as consisting of group molecules of hydrogen ( $\text{H}_2$ ) held together by carbon atoms. Chemical considerations, however, would lead us to choose  $\text{CH}_4$  as the group molecule.

In liquid methane we could distinguish the group molecule either by the fact that four atoms of hydrogen must be geometrically associated with a single carbon atom, or by the fact that four hydrogen atoms always move with a particular carbon atom, whereas all other neighboring hydrogen atoms in the course of time gradually (by diffusion) become separated more and more from the given carbon atom.

A crystal of zircon would thus be a compound consisting of group molecules of  $\text{ZrO}_2$  and group molecules of  $\text{SiO}_2$ .

In inorganic compounds in the solid or liquid state there are usually no fixed or group molecules. It is probable, however, that an ion of the type  $\text{CO}_3^-$  in solution constitutes a group molecule, since the structure of the calcite crystal suggests the carbon atom may be more or less permanently associated with three particular oxygen atoms. An ion of the type  $\text{OH}^-$ , however, can probably not be properly looked upon as a group molecule since the high mobility of the  $\text{OH}^-$  ion and other factors indicate that this ion is continually exchanging its atoms with the surrounding mass of water.

Besides these types of molecules, there are the large molecules which constitute colloid particles. These may be called *colloid molecules*. They probably usually consist of large aggregates of atoms or group molecules

combined together by means of secondary valence. In the second part of this paper the probable structure of these colloid molecules will be discussed in more detail.

Finally, every continuous solid or liquid mass whether homogeneous or not may be looked upon as consisting of one large molecule. We may speak of molecules of this type as *solid* or *liquid molecules*.

**Forces between Atoms in Crystals.**—From our knowledge of the structure of crystals and from such properties as specific heat, compressibility, thermal coefficient of expansion, elasticity in different directions, melting point, vapor pressure, and latent heat of evaporation, it should be possible to determine the laws governing the forces around the atoms. Such a study would give us the clearest kind of insight into the nature of chemical affinity.

In view of the marked influence of temperature on the properties of liquids and solids, it is evident that the motions of the atoms in solids are of great importance. A study of specific heats gives us considerable information regarding the kinetic energy of the atoms. According to the Principle of the Equipartition of Energy<sup>1</sup> the average kinetic energy of any particle is  $\frac{1}{2} kT$  for each degree of freedom, where  $k$  is the Boltzmann gas constant and is equal to  $1.372 \times 10^{-16}$  ergs per degree. In other words, each particle should contribute the amount  $\frac{1}{2} k$  to the specific heat for each degree of freedom which it possesses. Thus for a gram molecule of particles ( $6.06 \times 10^{23}$ ) we find a specific heat of  $\frac{1}{2} R$  for each degree of freedom. Here  $R$  is the gas constant ( $6.06 \times 10^{23} \times 1.372 \times 10^{-16} = 83.1 \times 10^6$  ergs/deg.). Expressed in calories this gives 0.993 calorie per degree per gram atom for each degree of freedom. We thus have the simple rule that the atomic or molecular heat should be numerically equal to 0.993 times the number of degrees of freedom ( $n$ ) of the atoms or molecules.

Each atom of a monatomic gas has three (translational) degrees of freedom and we should thus expect the atomic heat to be  $C_v = 3 \times 0.9935 = 2.98$ . Actually for all the monatomic gases we find exactly this value with the single exception of helium, which gives a slightly lower value.

The specific heats of most diatomic gases is approximately  $C_v = 5$ , from which we may conclude that there are five degrees of freedom (three translational and two rotational). The possible motion of the two atoms along the line joining them, evidently does not represent a degree of freedom. However, the diatomic gases like chlorine, bromine and iodine which are easily dissociated into atoms, have specific heats considerably greater than 5. There is thus evidence that with very strong chemical forces between atoms the number of degrees of freedom is less than with weaker forces.

<sup>1</sup> For a short description of this principle and its present significance, see Dushman, *General Electric Review*, Sept., 1914.

The atoms of copper, silver, gold and lead are arranged according to a simple face-centered lattice with single atoms at each point of the lattice. It is evident that there are no group molecules. Each atom must possess (at high temperatures) three degrees of freedom corresponding to the directions in which it may move.

We know, however, in accordance with Dulong and Petit's law that the atomic heat of these metals is approximately 6.0,<sup>1</sup> and this is usually explained by assuming that the atoms vibrate in such a way that their energy is equally divided between kinetic and potential energy. When a body such as a pendulum describes *harmonic* vibrations, the time average of its kinetic energy is equal to the time average of its potential energy, if we assume that its potential energy is zero when it passes through its equilibrium position. The equipartition principle is concerned directly only with kinetic energy, but if the average potential energy is equal to the average kinetic energy it is evident that it will contribute as much as the latter to the specific heat. Thus if the atoms of the solid body describe harmonic oscillations about their equilibrium positions, the atomic heat should be double that corresponding to the three degrees of freedom, in other words it should be  $6 \times 0.9935 = 5.96$ .

It is often said that in this case there are three kinetic and three potential degrees of freedom. This statement is open to serious objection, for it implies that the Equipartition Principle is applicable to potential energy. As a matter of fact, if the forces around the atoms are such as to lead to oscillations that are not harmonic in character there will in general be no equality between the time averages of the kinetic and potential energies. For example, let us consider a ball rolling on a surface, such as that represented in Fig. 1. If the ball is displaced from its lowest position and released, it will oscillate about this position. If the displacements are small the motion will be approximately

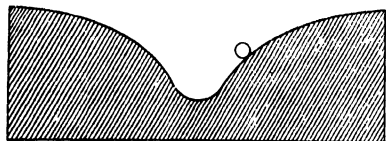


Fig. 1

harmonic in character. But with oscillations so large that the ball frequently mounts up on to the comparatively level parts of the surface, it is evident that the oscillations will be far from harmonic. In this case, the motion of the ball on the flatter parts of the surface will be

<sup>1</sup> According to Dulong and Petit's Law, the atomic heats of the elements at *constant pressure* are about 6.3. The specific heat of  $6 \times 0.993$  calculated by the Equipartition Principle is the atomic heat at constant volume. Lewis, Nernst, Lindemann and others have shown that the atomic heats of metals at *constant volume* gradually approach the above value asymptotically at higher temperatures, but at lower temperatures the atomic heat is considerably less. Elements with atomic weight less than about 20 form an exception to this rule in that their atomic heats are less than  $6 \times 0.993$  even at room temperature.

so slow that the length of time it remains in these positions will be much larger than it would be if the slope of the surface increased steadily from the center outwards. Thus with such a surface the time average of the potential energy may be much greater than the time average of the kinetic energy.

The same considerations apply to the oscillations of atoms. If the restoring force acting on an atom is proportional to the displacement from the equilibrium position (condition for harmonic motion) then the average kinetic and potential energies will be equal and the atomic heat will be  $6 \times 0.993$ . But if the restoring force increases more slowly than proportional to the distance (as in the case cited above), then the potential energy will be greater than kinetic energy so that by the Equipartition Principle the atomic heat will be greater than  $6 \times 0.993$ . On the other hand, if the restoring force increases more rapidly than the displacement, then the atomic heat will be less than  $6 \times 0.993$ .

The remarkable closeness with which the atomic heats at constant volume approach the value  $6 \times 0.993$  at the higher temperatures, may be taken as proof that the forces to which the atoms in solids are subjected vary approximately in proportion to the displacement of the atoms from equilibrium positions. There must then be both attractive and repulsive forces acting between the atoms. On the average, these opposing forces must just balance each other. As one atom approaches another the repulsive force must *gradually* increase and the attractive force decrease until the repulsive force greatly predominates. We cannot consider that the repulsive forces in solids are exerted only during collisions between atoms, for under these conditions there would be no potential energy and the atomic heat would be  $3 \times 0.993$ .

No adequate explanation has been offered of the repulsive forces between atoms. If matter is built up of positive and negative electricity the ordinary electromagnetic theory would indicate that the two opposite charges would neutralize each other. Actually, however, this neutralization only occurs to the extent of destroying the electric field at a comparatively large distance from the electrons. The positive and negative electrons are never able to destroy one another. Some cause, at present unknown, must operate to keep the positive and negative charges from approaching with less than a certain distance. It is evident that the laws governing the forces and motions of electric charges separated by distances comparable with the dimensions of atoms are in some respects radically different from the laws with which we are familiar. G. N. Lewis<sup>1</sup> believes that such considerations lead "irresistably to the conclusion that Coulomb's law of inverse squares must fail at small distances," and that it may be necessary to modify the law "even to the

<sup>1</sup> THIS JOURNAL, 38, 773 (1916).

extent of changing the sign of the force." This difficulty is undoubtedly connected in some way with those which have forced us to the quantum theory. Some more or less successful attempts have been made to apply this quantum theory to the structure of atoms and molecules. Bohr's theory of the hydrogen atom has been remarkably successful in that it enables one to calculate all the lines in the Balmer series of the hydrogen spectrum, but his theory of the hydrogen molecule is apparently not complete, for it leads to a value of 63000 calories for the heat of formation of  $H_2$  from atoms, while direct measurement<sup>1</sup> gives 84000 calories.

A very suggestive theory has been worked out by A. L. Parson<sup>2</sup> in which he assumes that the electron itself is not merely an electric charge but is also a magnet. Crehore<sup>3</sup> has developed a theory in which the magnetic field produced by the rotation of electrons in extremely small orbits ( $10^{-12}$  cm.) is assumed to play an essential part in the structure of molecules. By means of the magnetic fields, it is possible to account for both attractive and repulsive forces. Both of these theories assume that the positive electricity of the atom is distributed uniformly throughout a sphere of definite size, inside of which the electrons are located (Thomson's theory). Rutherford's work on the scattering of alpha particles, Moseley's work on X-ray spectra, and considerations based on the disintegration of the radioactive elements, all seem to compel us, however, to adopt Rutherford's theory of the atom in which the positive electricity is concentrated in the center of the atom and the electrons revolve in one or more orbits of diameters of the order of magnitude of  $10^{-8}$  cm. The strength of this evidence in favor of Rutherford's theory is such that it seems to the writer impossible to accept either Parson's or Crehore's theory in their present forms.

These questions will probably be satisfactorily answered only when we understand the mechanism underlying the quantum theory and know the true relationship between positive and negative electricity. We must have an explanation of the remarkable fact that the charge on an electron is *exactly* equivalent (although opposite in sign) to the unit of positive electricity (for example the nucleus of the hydrogen atom).

At present, therefore, in an analysis of the forces between atoms, we must recognize both attractive and repulsive forces, although we cannot satisfactorily explain the mechanism of the repulsive forces. Thus by admitting the existence of forces which prevent electrons from approaching too closely to positive charges we may accept Stark's and J. J. Thomson's theories of the general character of the forces between atoms.

<sup>1</sup> Langmuir, *THIS JOURNAL*, 37, 417 (1915).

<sup>2</sup> "A Magnetron Theory of the Structure of the Atom," *Smithsonian Publication* 2371, Washington, 1915.

<sup>3</sup> *Phil. Mag.*, 20, 310 (1915).

There are many other properties of solids which indicate that repulsive as well as attractive forces exist between atoms, and that the repulsive forces act over distances comparable with the dimensions of atoms and not merely during collisions between atoms.

The compressibility and coefficient of thermal expansion are two such properties. In the case of ideal gases, these quantities vary with the pressure and temperature in a way that indicates that the volume would be zero if the atoms or molecules were brought into contact.

From the smallness of the coefficient of expansion of solids we must conclude that even at the absolute zero of temperature, the volume of crystals would not be so very much less than at room temperature. Furthermore, there are no indications that the compressibility would become zero even at the absolute zero. These facts are further evidence that the atoms of solids tend to be held in definite equilibrium positions by forces which vary approximately proportionally to the displacements of the atoms from these positions.

Nernst, Einstein and Lindemann have shown that the natural frequency of vibration of the atoms of elements may be calculated by three independent methods based, respectively, on measurements of the specific heat at low temperatures, the compressibility and the melting point. The fairly good agreement between these methods lends further support to the belief that the atoms vibrate about equilibrium positions.

The intensity of the higher orders in the X-ray spectrum of crystals, increases as the temperature of the crystal is lowered. This effect, known as the Debye effect, constitutes striking proof of the heat vibrations of the atoms and should lead to quantitative measurements of these vibrations.

The magnitude of the heat conductivity of solids, especially metals, throws some interesting light on the character of atomic vibrations. Let us imagine all the atoms in the surface layer of a solid to have their temperature suddenly raised by a given amount. This layer will then rapidly cool and will approach the temperature of the underlying layers. The rapidity with which this temperature equalization takes place will measure the rate at which a motion of one atom affects the adjacent ones. A simple approximate calculation<sup>1</sup> gives for the time necessary for the temperature increment of the surface layer to fall to 37% of its initial value.

$$t_r = \frac{3k}{h\sigma} \quad (1)$$

Here  $k$  is the Boltzmann gas constant  $1.372 \times 10^{-16}$ ,  $h$  is the heat conductivity of the solid and  $\sigma$  is the distance between adjacent atoms. The quantity  $t_r$  is exactly analogous to Maxwell's "time of relaxation" in a gas which is the time needed for any abnormal distribution of kinetic energy among gas molecules to subside to  $1/e^{th}$  of its original value.

<sup>1</sup> See Langmuir, *Phys. Rev.*, 8, 149 (1916).

For copper we thus find  $t_r = 4.6 \times 10^{-16}$  seconds. This has been calculated on the assumption that each atom can receive heat from one direction only. When we consider that a single atom in the interior may receive energy from six different directions, it seems probable that the real time of relaxation of a single copper atom is about  $10^{-16}$  seconds. Now the atomic frequency calculated from the compressibility by Einstein's method is  $5.6 \times 10^{12}$ , or the time necessary for an atom to complete a single oscillation, the reciprocal of this or  $1.8 \times 10^{-13}$  seconds. Thus the time required for an atom nearly to reach equilibrium with its neighbors is only 1/1800th of the time of a single oscillation.<sup>1</sup>

Even for nonmetallic substances, such as sodium chloride, the time of relaxation is always very small compared to the natural period of the atoms. This indicates that motions of a single atom must always be very highly damped. In other words, the atoms behave towards each other as though they were almost completely inelastic. However, if all the atoms are stimulated simultaneously by a periodic disturbance having a frequency corresponding to the natural frequency of the atoms, then the oscillations will be practically undamped, for there are then no adjacent atoms to which the oscillating ones can give up their energy.

We shall see that this apparent inelasticity of the atoms of solids is of great importance in the theory of evaporation, adsorption and surface tension.

The principle of the Equipartition of Energy has been found to apply at higher temperatures to the specific heats of monatomic gases, most diatomic gases and most elementary solids. But at low temperatures the specific heats always fall below that calculated by this principle. According to Einstein's theory this is due to the inability of oscillators to take up energy in quantities less than  $h\nu$ , where  $h$  is Planck's quantum  $6.58 \times 10^{-27}$  erg deg. Whether this is the correct explanation or not, it is a fact that degrees of freedom tend to disappear at lower temperatures. Eucken has shown that at temperatures as low as  $58^\circ$  absolute, hydrogen molecules have only three degrees of freedom, whereas they have five at ordinary temperatures. Similarly the specific heat of helium at the lowest temperatures falls even below 2.98. Evidently, therefore, it is possible that a single atom may have less than three degrees of freedom, although it is hard for us to conceive of such a possibility.

<sup>1</sup> A. H. Compton, *Phys. Rev.*, 7, 341 (1916) in a "Physical Study of the Thermal Conductivity of Solids" reached the conclusion "that the average distance through which the energy of an atomic collision in a crystal is transmitted is approximately inversely proportional to the temperature and is many times the distance between atoms." In many ways this is equivalent to our conclusion that the time of relaxation is small compared to the natural period of oscillation. From what has been said above, Compton's statement is open to serious objection, since we cannot look upon the repulsive forces in solids as being due to collisions.



The smaller the atomic weight of an element and the greater the strength of the union between the atoms, the higher is the temperature at which the atomic heat begins to be normal (5.96). Thus there seems to be a relation between the natural frequency of the atoms and the deviations from the equipartition principle.

However, Trautz<sup>1</sup> attempts to explain the decrease in the specific heat of hydrogen at low temperatures by assuming that for each temperature a certain fraction of the hydrogen molecules are transferred into another modification of hydrogen which has the properties of a monoatomic gas. A. H. Compton<sup>2</sup> makes a somewhat similar assumption regarding solids, namely, that at low temperatures the atoms are agglomerated into larger aggregates in which the individual atoms lose one or more of their degree of freedom.

The specific heat of solids at ordinary temperatures is a distinctly additive property (Kopp's rule), a fact which is in itself an indication that solids are not built up of molecules. With compounds of the heavier elements, each atom contributes an equal amount (about 6.3 calories per gram atom at constant pressure) to the specific heat. In the case of the lighter elements, such as those forming organic compounds, the additive relations still hold fairly well, but the atomic heats of these elements must be taken to be less than 6.4. According to Kopp's rule,<sup>3</sup> the following atomic heats should be taken: C = 1.8, H = 2.3, B = 2.7, Be = 3.7, Si = 3.8, O = 4.0, P = 5.4, S = 5.4 and all elements of higher atomic weights about 6.4.

Accurate determinations of the specific heats of organic compounds in the solid, liquid and gaseous condition and at various temperatures will undoubtedly be of great service in establishing the character of the vibrations of the atoms and the nature of the forces controlling them. The available data at present are very meagre and unreliable.

**Chemical Compounds Existing Only in the Solid State.**—From what has been said regarding the relation between primary and secondary valences in solid bodies, it would follow that in general the composition of a solid body should give us little or no information about the primary valences. Conversely, we should expect more compounds to exist in the solid state than we would be led to predict from the ordinary rules of valence.

When we consider that every atom (and every molecule for that matter) is surrounded by a field of electro-magnetic force, it appears probable that solids can be built up with almost any arrangement of atoms, provided the temperature is sufficiently low. If these arrangements of

<sup>1</sup> *Verh. deut. physik. Ges.*, 15, 969 (1913).

<sup>2</sup> *Phys. Rev.*, 6, 377 (1915).

<sup>3</sup> Nernst, *Theoretische Chemie*, 1903, p. 180.

atoms are regular so as to constitute a space lattice, the resulting solid will have a definite and invariable chemical composition which can be represented by a chemical formula, and would, therefore, be recognized as a chemical compound. The arrangement of the atoms in such compounds would bear no more relationship to the primary valence of the atoms than does the arrangement of the carbon, oxygen and calcium atoms in a crystal of calcite. The formula representing a compound of this type would thus be totally unrelated to the valence of the atoms.

The reason that the composition of solid compounds is so often consistent with the ordinary valence rules, is probably that the compounds are formed from solutions or from gaseous phases. In liquids or gases there is naturally more opportunity for the primary valences to manifest themselves.

As a matter of fact there are vast numbers of chemical compounds which exist in the solid state only and among these compounds the absence of valence relations is very striking.

Tammann and his students have proven the existence of a hundred or more definite metallic compounds by their studies of alloys. Out of 100 such compounds only 26 have formulas which agree with the ordinary valence.<sup>1</sup> A few typical compounds are  $\text{AgMg}_3$ ,  $\text{AgMg}$ ,  $\text{AuZn}$ ,  $\text{Au}_3\text{Zn}_5$ ,  $\text{Cu}_3\text{Al}$ ,  $\text{CuAl}$ ,  $\text{CuAl}_2$ ,  $\text{Mg}_4\text{Al}_3$ ,  $\text{AlSb}$ ,  $\text{Zn}_7\text{Fe}$ ,  $\text{Zn}_3\text{Fe}$ ,  $\text{Al}_3\text{Fe}_2$ ,  $\text{NaZn}_{12}$ ,  $\text{NaCd}_5$ ,  $\text{NaHg}_4$ ,  $\text{NiCd}_5$ ,  $\text{AuSb}_2$ , etc. Tammann shows that definite compounds are never formed between metals which are closely related in the periodic system, such as Cu-Ag or Fe-Ni, although solid solutions or mixed crystals frequently form in these cases.

If we consider these metallic compounds from the viewpoint we have developed above, it is evident that the atoms are held together by secondary valence, as are for instance those in a copper crystal or a rock-salt crystal. The reason that they have a definite chemical composition is that the atoms are arranged in some form of regular lattice. For example, if, in a face centered cubic lattice such as that of a copper crystal, we should replace the corner atoms by atoms of an element A, and replace the atoms in the faces of the cubes by atoms B, then we should have a compound of the composition  $\text{AB}_3$ . Each atom A would be surrounded by twelve atoms B all equidistant. Each atom B, however, would have 4 atoms of A and 8 of B equidistant from it. Such a structure would reveal nothing as to the valency of the atoms. It is quite probable that the compound  $\text{AgMg}_3$  has a structure of this kind.

If the atoms of the copper crystal we have considered should be replaced by atoms of two elements A and B in an irregular manner, then the resulting crystal would not have a definite chemical composition and would, therefore, not be recognized as a chemical compound, but would be con-

<sup>1</sup> Tammann, *Z. anorg. Chem.*, **49**, 113 (1906) and **55**, 289 (1907).

sidered a solid solution or mixed crystal. Yet there is no reason to assume that the forces holding the crystal together in one case are any different from those in the other.

If the two elements have combined together to form a chemical compound in one case, why not assume that the elements are equally combined in the mixed crystal? In the crystal of a pure metal we should also consider the atoms chemically combined with one another.

In mixed crystals or solid solutions, the atoms are evidently arranged in a haphazard manner according to the laws of probability, many different arrangements of atoms occurring side by side in the crystal. If the atoms of the two elements differ sufficiently in size or in their fields of force, then certain of these arrangements will be more stable than others. Thus, although at low temperatures almost any conceivable arrangement of atoms might be stable, it may be impossible to form mixed crystals by cooling a molten mass, because the atoms during the process of solidification have ample opportunity to arrange themselves in the most stable arrangements.

Thus the limitation in the number of compounds actually found is probably due to the restrictions imposed by our present methods of preparing these alloys by solidification from a melt, and is not an indication that such chemical compounds (or solid solutions) are not capable of existence in the solid condition.

Mineralogy also affords us an abundance of compounds which exist in the solid condition only and whose composition is not in accordance with the ordinary valence rules. The complex silicates are apparently built up of compounds of the first order ( $\text{SiO}_2$ ,  $\text{K}_2\text{O}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{H}_2\text{O}$ , etc.) in much the same way that the metallic compounds are built up of the atoms of the metals. If we consider such typical compounds as  $(\text{K}_2\text{O})(\text{Al}_2\text{O}_3)(\text{SiO}_2)_6$ ;  $(\text{MgO})_3(\text{SiO}_2)_4(\text{H}_2\text{O})$ ;  $(\text{MgO})(\text{SiO}_2)(2\text{H}_2\text{O})_2$ , etc., it appears that the number of each of the groups ( $\text{K}_2\text{O}$ ), ( $\text{Al}_2\text{O}_3$ ), etc., which enter into the formula bears no relation to the valence of the elements. It is probable that in many cases each of the groups  $\text{K}_2\text{O}$ ,  $\text{Al}_2\text{O}_3$  really constitute group molecules and that these are held together in the crystal by secondary valence, just as the atoms of the metallic compounds are.

Solid solutions or mixed crystals are of even more frequent occurrence among minerals than among alloys, and similar considerations must apply in regard to their constitution.

In the field of inorganic chemistry, especially in that of complex salts so well covered by Werner and his students, the relative number of compounds that can exist in the gaseous condition is extremely small.

Practically all complex compounds decompose or dissociate when heated. Even sulfuric acid gives a vapor whose density indicates that it is completely dissociated into  $\text{H}_2\text{O}$  and  $\text{SO}_3$ . In fact the great majority of com-

plex compounds do not even show a molecular weight in solution which corresponds to their composition in the solid state. For example, when alum  $(K_2O)(Al_2O_3)(SO_3)_4(H_2O)_{24}$  is dissolved in water it shows a "molecular weight" very much less than that corresponding to its formula. Crystals containing water of crystallization cannot be made to evaporate and still retain the combined water.

The number of complex compounds that can be formed must be unlimited. If methods can be found for forming them at sufficiently low temperature, probably almost any conceivable arrangements of group molecules could be built up having definite chemical compositions. Or solid solutions consisting of almost any combination of atoms and molecules could theoretically be formed. We are only sharply restricted in the formation of compounds in the case of compounds of the first order. But there is no sharp limit to the compounds that may be formed by secondary valences.

So far we have considered only crystalline solid bodies. It is evident that atoms or group molecules could be arranged irregularly in space (not according to a regular space lattice). A solid body built up in this way would have the properties of an amorphous body or glass. There can be little reasonable doubt, but that the structure of glass is of this nature. Such a structure is naturally much more easily built up of group molecules than of atoms for the greater symmetry of the atom enables it to assume definite and regular positions with respect to its neighbors more readily than group molecules could do.

The nature of the forces acting between the atoms or group molecules in amorphous bodies cannot be essentially different from that in crystals. We should expect the union between adjacent atoms or molecules to be dependent upon exactly the same kind of chemical properties as those which determine the combination of the atoms or molecules to form complex compounds (secondary valence).

From the fact that glasses, when heated, change to the liquid state by a continuous process, we are led to conclude that the structure of a liquid does not differ from that of a glass in any essential respect except that in the liquid there is a certain mobility (entirely analogous to tautomerism). Therefore, even in a liquid we look upon every atom (or group molecule) as combined chemically (or adsorbed) to all the adjacent ones. The molecular weight is, therefore, a term that has very little significance in the case of a liquid. This theory of the structure of liquids will be developed in more detail in the second part of this paper.

#### STRUCTURE OF THE SURFACES OF SOLIDS.

Unfortunately the study of crystals by the X-ray spectrum has not yet given us any direct knowledge of the structure of the surfaces of solids. From the point of view of the chemist, the structure of the surface must be

of the utmost importance, for chemical reactions in which solids take part are practically always surface reactions.

Our knowledge of the surfaces of solids must, therefore, be derived from indirect sources.

Since the forces that hold the atoms of solids together are of the same kind as those that hold the atoms of complex chemical compounds, we have excellent reasons for believing that the forces decrease extremely rapidly as the distance between atoms increases. We may also draw this conclusion from the compressibility of solids.

The energy which must be expended in separating the atoms of a solid metal from each other is given by the latent heat of evaporation  $\lambda$  (per gram atom). We can also calculate the energy necessary to change the distance between atoms from the compressibility. By comparing this energy with the latent heat, we may estimate the distance through which atomic forces are effective.

Let  $K$  represent the coefficient of compressibility of an element having an atomic volume  $A/\rho$ . We have good reasons for believing that the atoms of a solid are subject to forces that vary in proportion to the displacement of the atoms from their equilibrium positions.<sup>1</sup>

If we compress a unit volume of a solid so as to decrease its volume by the amount  $\Delta V$  the work expended will be  $(\Delta V)^2/2K$ . If the body is subjected to tension in all directions (negative pressure) so as to *increase* its volume by the amount  $\Delta V$ , the work expended will also be  $(\Delta V)^2/2K$ . This relation will hold accurately only for such small negative pressures that  $K$  remains constant. It is evident that as the atoms are being separated from each other, the attractive forces will at first increase in proportion to the displacement, then gradually more slowly, until finally the attractive force reaches a maximum. Beyond this distance the force rapidly decreases (probably according to about the inverse 4th or 5th power) to negligible values. It will be very instructive, however, to calculate on the assumption that  $K$  is constant, how far we need to pull the atoms apart before the work expended will equal the known latent heat of evaporation.

We readily obtain

$$(\Delta V_0)^2 = \frac{2\lambda K}{A/\rho}.$$

<sup>1</sup> The specific heats and other properties of the heavier elements compel us to this view when the displacements are small. Richards has shown that the compressibility of the elements decreases gradually as the pressure is raised to very high values. This proves that the repulsive forces between atoms increase more rapidly than the displacement. It is well known that liquids can be subjected to negative pressures and have substantially the same coefficient of compressibility for negative as for positive pressures. Undoubtedly the coefficient  $K$  should increase considerably for very intense negative pressures. Nevertheless the assumption of a constant value of  $K$  could hardly affect to order of magnitude of the calculated range of atomic forces.

In this equation  $\Delta V_0$  represents the increase in volume which could cause an expenditure of energy equal to  $\lambda$  per gram atom. The volume is thus increased from 1 to  $1 + \Delta V_0$ . The relative increase in the distance between the atoms is given by  $\sqrt[3]{1 + \Delta V_0}$ . In Table I the data for several elements are given. According to Richards, tungsten is the least compressible and caesium the most compressible metal.

TABLE I.

Metal.	C. G. S. units.	$\lambda$ ergs.	$\lambda/p$	$\sqrt[3]{1 + \Delta V_0}$	$\bar{r}$ cm.	$\Delta \bar{r}$ cm.
W	$0.28 \times 10^{-12}$	$9.2 \times 10^{12}$	9.6	1.20	$2.8 \times 10^{-8}$	$0.57 \times 10^{-8}$
Pt	$0.38 \times 10^{-12}$	$5.4 \times 10^{12}$	9.1	1.19	$2.78 \times 10^{-8}$	$0.53 \times 10^{-8}$
Mo	$0.46 \times 10^{-12}$	$7.4 \times 10^{12}$	11.1	1.21	$2.96 \times 10^{-8}$	$0.62 \times 10^{-8}$
Hg	$3.95 \times 10^{-12}$	$0.58 \times 10^{12}$	14.8	1.16	$3.26 \times 10^{-8}$	$0.52 \times 10^{-8}$
Cs	$61.0 \times 10^{-12}$	$1.0 \times 10^{12}$	71.0	1.12	$5.50 \times 10^{-8}$	$0.66 \times 10^{-8}$

Thus, if the attractive forces between the atoms varied in proportion to the displacement, the expenditure of energy necessary to increase the distance between the atoms by 12% in case of caesium (or 21% in case of molybdenum) would be as great as that actually required to separate them to an infinite distance.

Actually, the attractive force can vary proportionally to the displacement only for displacements much less than 10% of the distance between atoms. However, the distance calculated by the above rough method is probably very close to that at which the *maximum attractive force* occurs. The work done in separating the atoms beyond this distance probably compensates for the decrease in attractive force before the maximum is reached.

From these considerations it seems safe to say that: *The attractive force between atoms reaches a maximum when the atoms are separated by distances 10-30% greater than the distance at which they are in stable equilibrium.*<sup>1</sup> Since the force varies with a high power of the distance, we may also conclude: *The attractive force becomes practically negligible when the distance between the centers of the atoms becomes twice as great as the distance at which the atoms are in equilibrium.*<sup>2</sup>

It is interesting to note in Table I that the values of  $\sqrt[3]{1 + \Delta V_0}$  are largest for the elements of smallest atomic volume. This suggests that the increase in actual distance at which the attractive force becomes a maximum may be approximately the same for all the elements. In the sixth column are given the distances between the centers of the atoms calculated from the atomic volume on the assumption that the atoms are arranged

<sup>1</sup> Grüneisen (*Ann. Physik*, 39, 298 (1912)) by a mathematical development of a theory of monoatomic solids concludes that the average *amplitude of vibration* of the atoms in a solid at its melting point is 8.5% of the distance between the atoms.

<sup>2</sup> Probably the best evidence of the very limited range of atomic forces is that afforded by surface tension phenomena. This will be discussed in the second part of the paper.

according to a face-centered cubic lattice. The next column gives  $\Delta\sigma$ , the increase in this distance corresponding to the increase in volume represented by  $1 + \Delta V_0$ . It is seen that the values of  $\Delta\sigma$  are substantially constant so that we may conclude that: *The attractive forces between atoms increase to a maximum when the distance between the atoms is about  $0.6 \times 10^{-8}$  cm. greater than the distance at which the attractive force is zero.*

We are now in a position to draw certain conclusions regarding the structure of the surfaces of crystals.

Let us consider a crystal such as calcite in which cleavage surfaces may be obtained. To break a crystal into two parts requires the expenditure of a certain amount of energy. Let  $\gamma$  be the *work or free energy* which must be expended in producing each square centimeter of cleavage surface. Thus if we have a crystal of one square centimeter in cross-section (parallel to a cleavage face),  $\gamma$  will be one-half of the work required to separate the crystal into two parts. In general  $\gamma$  will decrease as the temperature rises. If we consider the mechanism of the formation of a cleavage surface, it is evident that as the atoms are pulled away from each other a certain amount of work will be done by the thermal agitations of the atoms. The atoms moving towards the receding surface are repelled by a gradually decreasing force so that they return from the receding surface with a velocity lower (on the average) than that with which they started out. Thus there must be a certain cooling effect accompanying the formation of a cleavage surface and this heat energy must result in a corresponding decrease in the free energy required to produce the surface. This reasoning is entirely analogous to that in the case of the mechanism of the adiabatic expansion of a gas.

Simple thermodynamical reasoning (see first chapter of Nernst's *Theoretical Chemistry*) shows that in the production of a cleavage surface the amount of energy contributed by the thermal agitation is equal to  $-T d\gamma/dT$ . If we add to this the free energy expended, we obtain, for the total energy involved in the formation of a unit surface, the expression

$$\gamma_0 = \gamma - T \frac{d\gamma}{dT}. \quad (2)$$

This quantity  $\gamma_0$  represents the total potential energy of the surface. Since we look upon atomic forces as electromagnetic in nature, the quantity  $\gamma_0$  is a quantitative measure of the increase in the energy of the electromagnetic field surrounding the atoms, produced by the formation of the surface.

Just as we traced a relationship between the compressibility, the heat of vaporization and the range of atomic forces, we may derive a similar relationship between the elastic properties, surface energy and range of atomic forces. Unfortunately, however, few data on the surface energy of solids are available.

There is every reason for believing that the range of atomic forces is of the same order of magnitude in all the states of matter. In forming a cleavage surface, therefore, it is probable<sup>1</sup> that the atoms pull part when the distance between adjacent atoms has been increased by about  $0.6 \times 10^{-8}$  cm.

When electrically charged or magnetized bodies are brought into proximity, they tend to move in such a way that the total energy of the electric or magnetic field becomes a minimum. For example, if we imagine a number of small horseshoe magnets to be placed in a box and shaken, we should expect on opening the box to find that the magnets had become attached to each other in pairs in such a way that in each pair the north pole of one is in contact with the south pole of the other. This arrangement would be a very stable one and would require a maximum amount of energy to break it up.

In a similar manner the atoms in the surface of a crystal must tend to arrange themselves so that the total energy in the field surrounding them will be a minimum.<sup>2</sup> In general, this will involve a shifting of the positions of the atoms with respect to one another. However, from the fact that energy is always required to separate a solid body into two parts we must conclude that the field energy associated with the surface atoms is always greater than that associated with a like number of atoms in the interior of the solid, notwithstanding the shifting of the positions of the atoms in the surface layer.

The smallness of the range of the atomic forces, compels us to conclude

<sup>1</sup> Further evidence in support of this statement will be given in the second part of this paper.

<sup>2</sup> In the second part of this paper it will be shown that this principle is of great importance in connection with surface tension phenomena. The group molecules in liquids arrange themselves in the surface layer in such a way that the part of the molecule which has the weakest field around it actually forms the surface, while the more active parts of the molecule are drawn below the surface, and are then without effect on the surface tension except in so far as they crowd the surface atoms apart.

The above principle also seems to be related to the cleavage or crystal habits of solids. In a crystal built up of atoms arranged according to a face centered cubic lattice the number of atoms per sq. cm. of crystal face is  $5.56 \times 10^{15} \times V^{-\frac{3}{4}}$  for the 1:0:0 faces;  $4.02 \times 10^{15} \times V^{-\frac{3}{4}}$  for the 1:1:0 faces and  $6.57 \times 10^{15} V^{-\frac{3}{4}}$  for the 1:1:1 faces. Here  $V$  is the atomic volume. Thus the atoms are arranged more compactly in the octahedron faces than in any others.

For such faces the value of  $\gamma_0$  should be a minimum. When platinum is slowly sublimed at high temperatures as, for instance, in the winding of an electric furnace, it crystallizes in the form of beautiful octahedra. The writer has observed similar crystals of tungsten.

On the other hand, in the simple cubic lattice the most compact arrangement of the surface atoms occurs in the 1:0:0 faces. Crystals of the alkali halides have cubic cleavage and usually crystallize as cubes and the atoms in these crystals are spaced according to a simple cubic lattice.



that in general the distances through which the surface atoms are shifted from their original positions in the solid, are small compared to the average distance between atoms. We must also conclude that the abnormal surface arrangement is usually limited to the surface layer only.

The surface of a solid (or liquid), therefore, does not contain, as is usually assumed, a transition layer, consisting of several layers of atoms or "molecules," in which the density varies by continuous gradations from that of the solid to that of the surrounding gas or vapor. Instead we find that the change from solid to empty space is most abrupt. In a sense, the rearrangement of the atoms in the surface layer causes this layer to assume the character of a transition layer, but the density of the packing of the atoms in this layer is undoubtedly greater than in the body of the solid, so that there can be no gradual change in density from that of the solid to that of the space. Additional evidence in favor of this view will be given in the remainder of this paper.

The surface of a crystal must then consist of an arrangement of atoms as definite as that existing in the interior of the crystal, although slightly different from the latter. The surface must thus be looked upon as a sort of checker board containing a definite number of atoms, of definite kinds arranged in a *plane* lattice formation. The space between and immediately above (away from the interior) these atoms is surrounded by a field of electromagnetic force more intense than that between the atoms inside the crystal.

There are good reasons for believing that the intensity of this surface field of force is substantially independent of the temperature. The energy in the surface field is measured by  $\gamma_0$ . (Equation 2.) Now the work done, during the formation of a fresh surface by the thermal agitation of the molecules (namely,  $-T d\gamma/dT$ ), should be approximately proportional to the temperature. Therefore,  $d\gamma/dT$ , should be independent of the temperature. Thus we may place

$$\gamma = a - bT \quad (3)$$

where  $a$  and  $b$  are constants. Combining this with (2) we find  $\gamma_0 = a$ . In other words,  $\gamma_0$ , the total energy of the electromagnetic surface field should be independent of the temperature.

In the case of liquids, the free energy necessary for the formation of unit surface is called the surface tension. By analogy we would be justified in calling  $\gamma$  the surface tension of the solid. However, on the whole, it seems preferable with both solids and liquids to refer to the quantity  $\gamma$  as the *free surface energy* and  $\gamma_0$  as the *total surface energy*.

**Sublimation of Solids.**—Sublimation involves two processes; evaporation and condensation. Condensation being in some ways the simpler of the two will be considered first.

*Condensation of Vapors.*—When a crystal is in contact with its own saturated vapor the vapor must be continually condensing on the solid while the solid is evaporating at an equal rate. The rate at which the molecules of the vapor come into contact with the surface of the solid is given by the equation

$$m = \sqrt{\frac{M}{2\pi RT}} p, \quad (4)$$

where  $M$  is the molecular weight of the vapor,  $R$  is the gas constant,  $p$  is the pressure of the vapor and  $m$  is the rate at which the gas molecules strike against the surface, expressed in grams of vapor per sq. cm. per second.<sup>1</sup>

When a molecule of vapor strikes against the solid surface one of two things may happen. The molecule may be *reflected* from the surface, in other words, may rebound elastically, or it may *condense* on the surface, that is, it may be held by attractive forces in such a way that it forms at least temporarily a part of the solid body. It is of importance to know approximately what fraction of the molecules striking the surface are reflected.

In the kinetic theory of gases it has almost universally been assumed that molecules are perfectly elastic. This assumption has become so much a habit of thought that nearly everyone who has applied the kinetic theory to liquids and solids has taken it for granted that the collision between gases and surfaces of solids or liquids are also elastic.<sup>2</sup>

We have seen, however, from a consideration of the heat conductivity of solids that the time of relaxation of the atoms is usually small compared to the time necessary for the atom to complete a single oscillation. This means that before an atom can be displaced a perceptible distance the energy causing the displacement has been dissipated among all the adjacent atoms. From this fact it appears that the collisions of molecules against solid bodies must in general be almost wholly inelastic.

In a recent paper in the *Physical Review*<sup>3</sup> the writer has discussed this question very fully, and gives abundant evidence both experimental and theoretical, for the inelasticity of the collisions between gas molecules and solid surfaces. There are apparently some cases in which a moderate

<sup>1</sup> This equation is a simple modification of the equation giving the rate of effusion of gases through small openings (Meyer's Kinetic Theory of Gases, German edition, 1899, p. 82). Its derivation was given by the writer in an article in the *Phys. Rev.*, **2**, 331 (1913). The importance of this equation in the kinetics of heterogeneous reactions can hardly be over-emphasized. See for example Langmuir, *THIS JOURNAL*, **37**, 1144 (1915).

<sup>2</sup> N. T. Bacon (*J. Phys. Chem.*, **17**, 762 (1913)) suggests that molecules are not elastic, and in this way explains qualitatively the phenomena of adsorption and catalytic action.

<sup>3</sup> *Phys. Rev.*, **8**, 149 (1916).

amount of real reflection does occur, but these cases must be looked upon as the exception rather than the rule.

According to this viewpoint the mechanism of the condensation of a vapor on a solid is as follows:

In the vapor surrounding the solid, the average distance which the molecules travel between collisions (the mean free path) is of the order of magnitude of  $10^{-5}$  cm. if the pressure is atmospheric, while it is correspondingly greater if the pressure is less. When a vapor molecule approaching the surface comes within a distance of about  $2 \times 10^{-8}$  cm. of the surface layer of atoms it begins to be acted upon by the electromagnetic field close to the surface. The vapor molecule thus experiences a force attracting it towards the surface. As it moves closer to the surface the attractive force rapidly increases and soon reaches a maximum intensity. The attractive force then rapidly decreases, and falls to zero when the molecule has traveled a distance only about  $0.6 \times 10^{-8}$  cm. beyond the point at which the force was a maximum. The point at which the force falls to zero may be regarded as an equilibrium position. When the molecule reaches this position its kinetic energy will be very high for a relatively large amount of work has been done upon it by the attractive forces. It will, therefore, not remain in the equilibrium position, but will move still closer to the atoms of the solid, and will thus enter a region in which it is subjected to very strong and rapidly increasing repulsive forces. If the molecule had lost no energy to adjacent atoms it would probably travel a distance  $0.2-0.3 \times 10^{-8}$  cm. against these repulsive forces before being brought to rest. It would then pass again through the equilibrium position and finally out through the region of attractive forces, and might thus again escape from the surface forces, in other words, be reflected.

But the improbability of such a reflection is evident when we consider the ease with which energy is dissipated to adjacent atoms. This energy loss occurs in two ways. In the first place, when the molecule is approaching the surface, the attractive force is exerted by *several atoms* on the surface. These atoms are thus all accelerated towards the incident molecule. A little later when the molecule is in the region of repulsive forces, these forces will be exerted principally by a *single atom* of the solid. The energy used in accelerating the surface atoms can, therefore, only partially be delivered back to the incident molecule. This dissipation in energy, even if only relatively small, will usually make it impossible for the molecule to pass out through the region of attractive forces.

The second kind of loss of energy, which is probably the more important, is that which causes the remarkably small time of relaxation in solid bodies. We have seen that in the interior of crystals the time taken for adjacent atoms to reach thermal equilibrium with each other is of the order of  $10^{-16}$  seconds. The duration of a collision between a molecule and a surface

(that is, the time between successive passages through the region of maximum attractive force) must be of the order of  $10^{-13}$  seconds. Thus in general, the energy delivered to the incident molecule by the attractive forces, is practically wholly dissipated to the adjacent atoms by the time the molecule first reaches the equilibrium position. It, therefore, has not sufficient kinetic energy to enable it to penetrate far into the region of repulsive forces, and certainly not sufficient to allow it to work against the attractive forces and thus escape from the surface.

The condensation of a vapor on a solid surface thus takes place independently of the temperature of the surface.<sup>1</sup>

This is especially evident when we consider that the intensity of the field of force close to the surface, as measured by the total surface energy  $\gamma_0$ , is itself independent of the temperature. The rate of evaporation on the other hand varies extremely rapidly with the temperature.

If practically every molecule of vapor which strikes against the surface of the solid condenses, it is not at first evident how the molecules, especially if they are complex, are able to arrange themselves to form a crystalline mass. In analyzing the mechanism of condensation we must distinguish two extreme sets of conditions that may occur. These may be termed *irreversible* and *reversible* sublimation.

By *irreversible* sublimation I mean the type which occurs for instance when a tungsten filament is heated to a high temperature in a well evacuated bulb. Under these conditions there can be no equilibrium, for the bulb is at a temperature thousands of degrees lower than that at which the vapor can be produced. The vapor is thus enormously superheated with respect to the surface on which it condenses. Such conditions as this can only be realized in practice when the vapor is at very low pressure, for, otherwise, the amount of vapor condensed per unit area per second would be so great that the heat liberated by the condensation could not be removed rapidly enough to maintain a low temperature on the condensing surface.

By the term *reversible* sublimation we may designate that which takes place for example, when iodine or naphthalene is sublimed slowly at ordinary temperatures.

In this case we are dealing with small differences of temperature, and we shall see that under these conditions condensation and evaporation are going on simultaneously at nearly equal rates over every portion of the surface where condensation occurs.

The mechanisms of reversible and of irreversible sublimation are in some ways quite different, and from the experimental side the phenomena show marked distinctions.

<sup>1</sup> It must of course be remembered that what we ordinarily observe during the condensation of a vapor is the difference between the rate of condensation and the rate of evaporation.

In the irreversible sublimation the vapor molecules remain where they first strike the surface, since they can neither be reflected nor re-evaporated. The deposit formed by the condensed vapor is, therefore, homogeneous (when gaseous impurities are absent) and is of uniform thickness. If the temperature of the surface on which condensation occurs is sufficiently low, the deposit will be wholly noncrystalline, since the atoms or molecules become rigidly fixed in position when they strike the surface and thus have no opportunity to arrange themselves as in a crystal. With the condensing surface at higher temperatures, however, a sintering or crystallizing process may go on within the deposit even when the temperature is below that at which perceptible vaporization occurs.

By means of this irreversible sublimation it is possible to obtain any volatile body in a noncrystalline form.

In the case of reversible sublimation the deposit formed from the condensed vapor is ordinarily very crystalline, frequently consisting of groups of separate crystals. In the formation of these crystals every molecule of vapor which strikes the surface condenses just as in the case of irreversible condensation, but most of these molecules re-evaporate again. The tendency of different molecules to re-evaporate will depend entirely on how firmly they are held by the atoms of the crystal. Thus the molecules which strike the surface in such a way as to form a continuation of the space lattice already present, will evaporate much less frequently than molecules which are not in positions where they can fit in with the crystal structure. The continual evaporation and condensation going on over the whole surface of the crystal allows the atoms to arrange themselves in the most stable positions. The smaller the differences in temperature and the more nearly equal the rates of condensation and evaporation, the more perfect will be the development of the crystals.

*Evaporation of Solids.*—We have seen that the condensation of vapors on a solid body takes place at a rate which is practically independent of the temperature. The rate of evaporation, however, increases rapidly with temperature.

Since evaporation and condensation are in general thermodynamically reversible phenomena, *the mechanism of evaporation must be the exact reverse of that of condensation*, even down to the smallest detail.

In the condensation of a monatomic vapor such as that of a metal, each atom as it approaches the surface comes into a region in which it is attracted. It is thus accelerated, but it gives up its newly acquired energy to adjacent atoms nearly as fast as it receives it. It soon reaches a region of repulsive forces, and is then brought to a stop. It then continues to move about an equilibrium position with an irregular motion due to thermal agitation.

Conversely in the evaporation of an atom of a metal the atom must

acquire energy from adjacent ones and thus be accelerated outward. As it moves it must receive successive increments of energy from its neighbors until finally it passes out of the region of attractive forces. From the smallness of the time of relaxation we are thus compelled to believe that an atom only escapes when it thus receives a very large number of successive impulses from the adjacent atoms.

The very small probability of such a sequence of favorable impulses is the reason that so few atoms evaporate at lower temperatures.

We may picture to ourselves the mechanism of evaporation by imagining a large number of heavy balls suspended (according to a two-dimensional lattice) from a ceiling by steel springs. Each ball is to be coupled to each of its neighbors by springs under tension. If some of the balls are set in motion the energy will be rapidly propagated to the others so they will all be in a state of agitation. To properly imitate the structure of a solid the coupling between the balls should be so stiff that the total energy of one ball can be transmitted to its neighbors in a very small fraction of the time required for a single oscillation.

When all the balls have been in motion long enough for a steady state to have been reached the velocities will be distributed among them according to the probability laws, in other words, according to Maxwell's distribution law.

If the springs are of brittle wire so that they snap when elongated more than a certain amount, then from time to time balls which have acquired an unusually large downward displacement will break their springs and escape. This will be quite analogous to evaporation.

The rate of evaporation of a solid is thus determined by the number of surface atoms per second which reach a certain critical condition. By means of Maxwell's distribution law it can thus be readily shown<sup>1</sup> that the rate of evaporation should increase with the temperature according to an equation of the form

$$m = A\sqrt{T} e^{-\lambda/RT} \quad (5)$$

where  $\lambda$  is the internal latent heat of evaporation per gram atom, and  $A$  is a constant whose value will depend primarily on the degree of coupling between adjacent atoms.

In the study of the disintegration of radioactive substances it has been

<sup>1</sup> Richardson (*Phil. Trans.*, 201, 516 (1903)) calculated in this way the rate of evaporation of electrons from heated metals (thermionic emission). The derivation of Equation 5 is also given by the writer (*THIS JOURNAL*, 35, 122 (1913)) in connection with a study of the reaction between oxygen and tungsten at high temperatures. It was also pointed out that this equation is substantially equivalent to Arrhenius' equation for the temperature coefficient of reaction velocity.

The significance of Maxwell's distribution law in relation to the kinetics of chemical reactions has been very fully treated in a recent paper by R. Marcellin (*Annales de Physique*, 3, 185 (1915)).

customary to speak of the life or period of the atom. In a similar way we may calculate the "life" of an atom on the surface of an evaporating solid.

The number of atoms evaporating per second per sq. cm. of surface will be  $Nm/M$  where  $N$  is the Avogadro constant and  $M$  is the atomic weight of the substance. If  $N_o$  is the total number of atoms per sq. cm. of surface then  $t$ , the average live of an atom on the surface will be

$$t = \frac{N_o M}{Nm}. \quad (6)$$

The "half period," that is, the time which must elapse before half of any selected lot of atoms will have evaporated, is equal to

$$t_{1/2} = 0.693 \frac{N_o M}{Nm}. \quad (7)$$

We have just seen that the constant  $A$  in Equation 5 is dependent on the coupling between the atoms. The time of relaxation of the atoms is also a measure of this coupling. It should thus be possible to estimate the time of relaxation from the rate of evaporation, and it will be of interest to see how the result calculated in this way compares with that found from the heat conductivity.

We see from Equation 5 that the rate of evaporation,  $m$ , depends on the latent heat of evaporation. If we substitute  $\lambda = 0$  in Equation 5 we obtain a hypothetical value of  $m_o$  (let this be  $m$ ), that represents the rate of evaporation which would occur if attractive forces did not prevent the escape of atoms from the surface. Thus we obtain from (5)

$$\frac{m}{m_o} = e^{-\lambda/RT}. \quad (8)$$

By Equation 6 the average life of an atom on the surface of a solid evaporating at the rate  $m_o$ , is

$$t_o = \frac{N_o M}{Nm_o}. \quad (9)$$

Eliminate  $m_o$  between (8) and (9).

$$t_o = \frac{N_o M}{Nm} e^{-\lambda/RT}. \quad (10)$$

Or from (5)

$$t_o = \frac{N_o M}{NA\sqrt{T}}. \quad (11)$$

The quantity  $t_o$  thus represents the average length of time an atom would remain on the surface if there were no attractive forces to hold it. Now the "time of relaxation" has been defined as the time required for an atom to give up all but  $1/e^{th}$  of its excess energy to adjacent atoms. It is evident that the time required for an atom at rest to be set in motion

will also be measured by the time of relaxation. Thus  $t_0$  should be of the same order of magnitude as the time of relaxation, and probably only differs from it by some constant factor not very far from unity.

The rates of evaporation of tungsten<sup>1</sup> platinum and molybdenum<sup>2</sup> in a very high vacuum, have been measured by Mr. G. M. J. Mackay and the writer. The values of  $t_0$ , calculated from these data by Equation 10 are given in Table II.

TABLE II.

	W.	Mo.	Pt.
$N_0$ .....	$1.46 \times 10^{16}$	$1.32 \times 10^{16}$	$1.51 \times 10^{16}$
$t_0$ at $300^\circ \text{K.}$ .....	$3.4 \times 10^{-19}$	$3.5 \times 10^{-20}$	$1.1 \times 10^{-16}$
$t_0$ at $2000^\circ \text{K.}$ .....	$5.2 \times 10^{-18}$	$1.0 \times 10^{-18}$	$3.0 \times 10^{-16}$
$t_r$ by Equation 1.....	$1.3 \times 10^{-16}$	.....	$2.3 \times 10^{-18}$

For comparison, the "times of relaxation"  $t_r$  calculated by Equation 1, are given in the last line. It will be remembered that Equation 1 gives too high a value for  $t_r$  because it was assumed in its derivation that an atom could take up energy only from atoms in one given direction. It is seen that the order of magnitude of  $t_0$  is not very different from that of  $t_r$ . We must not expect any very good agreement between  $t_0$  and  $t_r$  because of the very great effect of slight errors in  $\lambda$  on the value of  $t_0$  calculated by Equation 10. Thus if  $\lambda$  is taken one per cent. too large the value of  $t_0$  will be 20 times too small. On the whole, therefore, we may conclude that the values of  $t_0$  calculated as above, furnish confirmatory evidence that the time of relaxation of the atoms in solids is hundreds if not thousands of times smaller than the "natural period" of atomic vibrations.

So far we have considered the evaporation of solids which give monatomic vapors. When a crystal such as sodium chloride evaporates the atoms must group themselves together in pairs *before* they escape from the surface forces.

The latent heat of evaporation does not correspond to the energy required to separate the atoms from each other, but only to the energy needed to separate one group of atoms from other similar groups. This makes it appear that evaporation in these cases is the result of a tautomeric change taking place among the surface atoms. Thus in the case of solid sodium chloride the sodium atoms are ordinarily held to the adjacent chlorine atoms by secondary valence. If, however, a tautomeric change occurs by which a pair of adjacent chlorine and sodium atoms becomes attached to each other by *primary* valences, then this pair will be held to the surface by much weaker forces than those holding other atoms not so combined. The pairs held by primary valences may thus be enabled to evaporate from the surface. We should not assume, however, that

<sup>1</sup> *Phys. Rev.*, **2**, 329 (1913).

<sup>2</sup> *Ibid.*, **4**, 377 (1914).



every pair of atoms so combined, or even the majority of them, will evaporate, for if we do, it would follow that only a very small fraction of molecules of salt vapor striking a surface would condense. It is more likely that the tautomeric changes take place with high frequency, but that the time during which a pair of atoms exists consecutively in the tautomeric form is comparable with the time of relaxation, that is, of the order of  $10^{-17}$  seconds. Now the time required for an atom or a group of atoms to move out of the region of attractive forces (a distance of about  $10^{-8}$  cm.) must be at least  $10^{-14}$  seconds, since molecular velocities are always less than  $10^6$  cm. per second. We are thus led to believe that a sodium chloride molecule only evaporates when the tautomeric change occurs at a moment when the atoms are already displaced from their equilibrium positions to an unusual degree.

The evaporation of compound substances of the polar type thus involves rather complicated chemical changes in which the atoms rearrange themselves according to their primary valences. This conception of the mechanism of evaporation receives support from the fact that so few complex polar compounds or molecular compounds can be volatilized without dissociation. Thus nearly all inorganic salts except those which are compounds of the first order (halide salts for instance) are decomposed or dissociate on heating. Crystals containing water of crystallization can never be distilled with their water of crystallization. Even compounds like sulfuric acid give vapors which are dissociated.

Nonpolar compounds, such as most organic substances, usually contain fixed molecules which, even in the solid condition, are held together by primary valences, the secondary valences merely serving to hold the fixed molecules together. In this case evaporation involves only a breaking of the secondary valence forces so that it becomes quite similar to the evaporation of metals or other substances giving monatomic vapors.

*Relation between Condensation and Evaporation.*—When a solid is in equilibrium with its own vapor, condensation and evaporation are occurring simultaneously at equal rates. We have seen that we are justified, in the majority of cases, in considering that all the molecules of vapor which strike against the surface condense (are not reflected). Now the rate at which the molecules strike the surface is given by Equation 4

$$m = \sqrt{\frac{M}{2\pi RT}} p. \quad (4)$$

Since all of the molecules condense, and since the rate of evaporation must be equal to the rate of condensation, we may use this same equation to calculate the rate of evaporation,  $m$ , in terms of the pressure  $p$ , of the saturated vapor. If the condensation and evaporation go on independently of one another, then Equation 4 should give a means of calculating the rate at which a solid evaporates into a perfect vacuum. Or

conversely if we determine the rate of evaporation of a solid in a high vacuum we can calculate the vapor pressure by the above equation.<sup>1</sup>

This theoretical relation between the rate of evaporation and vapor pressure was first obtained by Hertz.<sup>2</sup> Hertz himself and others who have used the equation have not considered that the reflectivity is negligible and hence looked upon the calculated value of  $m$  as being greater than the true rate of evaporation.

R. Marcellin<sup>3</sup> has recently attempted to measure the maximum rate of evaporation of naphthalene, nitrobenzene and iodine, in a vacuum, and compares his results with those calculated by Equation 4. He concludes that at 40° only about one molecule out of 20 striking the surface condenses, while at 70° about one out of five condenses. That is, the reflectivity decreases rapidly at higher temperatures. It should be noted on the other hand that R. W. Wood<sup>4</sup> finds no reflection of mercury atoms from a surface at very low temperatures but concludes that the atoms are all reflected at higher temperatures.

Marcellin measured the rates of evaporation of substances in capillary tubes. By plotting the rate of evaporation against the length of the tube through which the vapor had to pass, he *extrapolated* back to zero length of tube, and expected in this way to find the rate of evaporation in a perfect vacuum. When we consider that this extrapolation was carried out over a length of tube at least eight times the diameter of the tube, we realize how very few of the molecules evaporating from the surface could have escaped, from the end of the tube. The great majority of them must have struck the walls of the tube and thus have been afforded an opportunity of returning back onto the surface. Measurements of this sort, to have any value, must be made so that molecules evaporating from the surface may move off in straight lines without meeting any obstruction until they strike the cooled surface on which they permanently condense.

If Marcellin had plotted the reciprocal of the speed of evaporation (which should be a linear function of the length of the tube) instead of the speed itself, it would have been apparent, first that the observed rates were much lower than the true maximum rates, and second, that even with the small capillaries he used he did not succeed in keeping the temperature of the evaporating surface up to that of the bath surrounding the tube. Therefore, it appears that Marcellin's experiments are entirely

<sup>1</sup> The writer, together with Mr. G. M. J. Mackay, has used this method for measuring the vapor pressures of the metals tungsten, platinum, molybdenum, iron, nickel, copper and silver, and the results have been, or will be, published in the *Physical Review*. The reasons which justify the assumption that the reflectivity is negligible, are given in detail in a recent article (*Phys. Rev.*, 8, 149 (1916)).

<sup>2</sup> *Ann. Physik*, 17, 177 (1882).

<sup>3</sup> *Annales de Physique*, 3, 185 (1915).

<sup>4</sup> *Phil. Mag.*, 30, 300 (1915).

consistent with the view that the true rate of evaporation is accurately given by Equation 4.

The writer has also shown<sup>1</sup> that Wood's experiments may equally well be explained by assuming, instead of a reflection of mercury atoms, at the higher temperatures, a condensation followed by evaporation.

For the case of a clean surface of liquid mercury evaporating into a good vacuum Knudsen has recently<sup>2</sup> proved that Equation 4 gives the actual rate of evaporation.

Wood makes the statement that atoms of mercury which are "diffusely reflected" (or according to our theory, condensed and re-evaporated) from a surface, do not seem to be distributed quite according to Lambert's cosine law, but there seem to be too few atoms leaving the surface in directions nearly parallel to the surface. Now if evaporation and condensation can go on simultaneously, although independently, it must follow, according to Maxwell, that the number of atoms leaving the surface in different directions must be proportional to the projected area in that direction (Lambert's cosine law).

Observations on the evaporation of metals in high vacuum have convinced the writer that Lambert's cosine law does hold accurately for evaporation, and the Wood's conclusion is incorrect.

Wood drew his conclusions from the *apparent* sudden decrease in the thickness of a film of metal deposited on glass, in the region close to the plane of the surface from which "reflection" took place. In the writer's experience, this sudden decrease which he has often observed, and which certainly seems very real, is only apparent. It is due to the fact that, although the *thickness* of the film varies *linearly* with the distance from the plane of the surface, the *light absorption* varies *exponentially*.

Kaye and Ewen<sup>3</sup> have reported that at pressures of a few mm. of gas, the sublimation from heated metals (Fe, W, Cu, Ag or Ir) appear to consist of two parts, one of which, diffuses like a gas, but the other, often the larger part, is projected in straight lines in a direction perpendicular to the surface at which it originates. In the experience of the writer such effects are due to convection currents (which often produce very freakish effects at pressures of a few mm.) or to electric discharges through the gas. They are usually enormously stimulated by the presence of traces of moisture. In a thoroughly dry gas or in a good vacuum, and in the absence of electric discharges, the evaporation of heated metals takes place without any evidences of such "projection" of particles in definite directions. Of course in a really good vacuum the atoms leaving the heated surface, travel in perfectly straight lines until

<sup>1</sup> *Phys. Rev.*, *loc. cit.*

<sup>2</sup> *Ann. Phys.*, **47**, 697 (1915).

<sup>3</sup> *Proc. Roy. Soc.*, (A) **80**, 58 (1914).

they strike an obstacle, and in this way "shadows" of interposed objects may be obtained. But this projection of particles takes place according to Lambert's cosine law and is in full accord with the ordinary conceptions of the kinetic theory.

We have assumed so far that evaporation and condensation can go on simultaneously without influencing each other. For example, in calculating by Equation 4 the rate of evaporation in a vacuum from the pressure of the saturated vapor, we had to assume that the true rate of evaporation in presence of saturated vapor is the same as that in vacuum, in other words, that the condensation of the vapor has no effect on the rate of evaporation.

There are, however, reasons which might lead us to expect a difference in the rate of evaporation in presence of and in the absence of vapor.

In the first place, when a vapor atom or molecule condenses on a surface an amount of energy corresponding to the latent heat of evaporation must be liberated, and must result in a local rise of temperature. It would seem that this might cause the evaporation of an adjacent atom which would otherwise not evaporate. Thus the condensation of vapor might stimulate the evaporation. This would be equivalent in many ways to a reflection of vapor molecules from the surface.

The following considerations make it very improbable that condensation has any such effect on evaporation. The "average life" of an atom on a surface may be readily calculated from Equations 4 and 6. The life will be inversely proportional to the vapor pressure, and will be proportional to  $\sqrt{MT}$ . If we choose  $M = 25$ ,  $T = 400$  and  $p =$  one megabar (atmospheric pressure) and assume that  $N_0 = 10^{16}$  atoms per sq. cm. we thus calculate that the life of an atom on the surface would be  $3.8 \times 10^{-9}$  seconds. In the evaporation of substances in vacuum the equilibrium pressure would always be extremely small compared to one megabar, so that the life of the atoms on the surface would be much more than  $10^{-8}$  seconds. Now the time taken by an atom to receive or give up its energy to adjacent atoms is of the order of  $10^{-17}$  seconds, or about  $10^{+9}$  times less than the life of the atom on the surface. These figures show that the critical conditions necessary to cause the evaporation of an atom are of relatively rare occurrence. The chance is negligibly small, therefore, that an atom condensing on the surface will be able to give up its energy to an adjacent atom at a moment when the latter is nearly in its critical condition.

These considerations make it appear probable that the energy liberated by the condensation of vapor is totally without influence on the mechanism of evaporation.

There is, however, another kind of effect by which condensation may, and probably does, influence the rate of evaporation. Let us consider

for example solid naphthalene in contact with its saturated vapor. When a molecule of naphthalene vapor strikes against the surface of the crystalline substance it undoubtedly condenses in the position in which it strikes. The chances are small that this position will be one in which the molecule forms a continuation of the space lattice of the crystal. If the temperature is sufficiently high the molecule may, by a sort of sintering process, readjust its position in conformity with the underlying group of molecules. But at lower temperatures this readjustment will often be impossible.

Such irregularly placed molecules will tend to evaporate from the surface more rapidly than those in the regular lattice positions.

We have already seen that this greater rate of evaporation manifests itself in the tendency for larger and more perfect crystals to be formed, as the sublimation of a substance is made more nearly reversible.

Since the rate of evaporation of the irregularly placed molecules must be finite, it follows that the surface must be more or less completely covered by such molecules. In other words, the surface of a crystalline solid in equilibrium with its saturated vapor may be covered by a layer of irregularly placed molecules, in other words, there may be an amorphous surface film.

The extent to which the surface is covered by such a film will depend upon the ease with which the molecules rearrange themselves, and also upon the relative rates of evaporation of the regularly and irregularly placed molecules.

It is of interest to consider the evaporation and condensation of a crystal of naphthalene under various conditions:

1. *Irreversible Condensation.*—If a stream of naphthalene vapor is admitted at low pressure into a well exhausted bulb immersed in liquid air, we should expect that all the molecules would condense in the positions in which they first strike the cooled bulb. The condensed material should then be wholly amorphous, both on its surface and in its interior.

2. *Irreversible Evaporation.*—If a naphthalene crystal is suspended in an exhausted bulb and the latter is immersed into liquid air, the naphthalene crystal will evaporate irreversibly, since no molecules of naphthalene will return from the surface of the bulb. In this case there will be no amorphous surface layer on the crystal.

3. *Reversible Evaporation or Condensation.*—If a naphthalene crystal is placed in one arm of an inverted and exhausted U-tube and the other arm is maintained at a very slightly lower temperature, the naphthalene will slowly sublime from one arm to the other, and form crystals in the cooler arm. These crystals as well as the one in the warmer arm will have amorphous surface layers.

If we calculate the rate of evaporation from the pressure of the saturated vapor by Equation 4 we obtain a value which corresponds to the rate

of evaporation from the amorphous surface layer, and not from the true crystalline surface. Therefore, the rate of evaporation of a crystal in a good vacuum (Case 2, Irreversible Evaporation) should be lower than that calculated from the vapor pressure, notwithstanding the fact that no reflection of molecules from the surface takes place.

It is probable that in the great majority of cases, especially with substances such as metals which give monatomic vapors, that this effect is entirely negligible, because of the great ease with which the atoms can arrange themselves on the surface.<sup>1</sup>

Even with substances having molecules as complicated as that of naphthalene it seems improbable that the difference between the rates of evaporation of crystalline and amorphous surfaces would be great enough to very seriously affect the validity of Equation 4, when applied to the calculation of the rate of evaporation in a vacuum. Accurate experimental determinations of the rates of evaporation of complex organic compounds in high vacuum should prove of great interest.

There are cases, however, where we may expect very radical differences between the true rates of evaporation *in vacuo* and the rate calculated from the vapor pressure by Equation 4.

Red phosphorus should furnish an example of this sort. The transformation of yellow into red phosphorus takes place very much more slowly than the rate at which molecules of phosphorus vapor strike against a surface of red phosphorus. Therefore, the molecules of phosphorus vapor which impinge against the surface and condense, must evaporate again without having been in the condition of red phosphorus.

The surface of the red phosphorus is, therefore, covered, at least in part, by a layer of fixed molecules which constitute an adsorbed film of yellow phosphorus. The rate of evaporation calculated by Equation 4 corresponds to the evaporation from this adsorbed film of yellow phosphorus plus that from the uncovered portion of the surface of red phosphorus. On the other hand if the red phosphorus is placed in a good vacuum the adsorbed film of yellow phosphorus will distill off and the observed rate of evaporation will correspond to the rate of conversion of

<sup>1</sup> According to the principle already enunciated, by which every element in the mechanism of a reversible process must itself be reversible, it follows that any rearrangement of molecules on the surface, which takes place during the condensation of a vapor, must take place to the same extent, but in the reverse direction, in the evaporation of the substance. Thus if molecules rearrange themselves into regular positions, an equal number of molecules must be continually leaving regular positions to assume irregular positions. This leads to the conclusion that even with substances which give monatomic vapors, the surface must in part be amorphous. However, an amorphous structure due to this cause will be present to the same extent when the evaporation is irreversible as it is in the case of reversible evaporation. Therefore no error is made in calculating the rate of evaporation in a vacuum from the vapor pressure, according to Equation 4.

red into yellow phosphorus. This rate will be very much less than that calculated from the equilibrium pressure.

It is thus probable in the case of red phosphorus that the equilibrium pressure is not a true vapor pressure in the ordinary sense, but is rather to be regarded as a dissociation pressure.

The rate of evaporation of ammonium chloride in a vacuum, both in the presence of and in the absence of traces of moisture, should throw a very interesting light upon the mechanism of the evaporation or dissociation<sup>1</sup> of this substance.

### The Dissociation of Solids and the Kinetic Interpretation of the Phase Rule.

Sometime ago it was pointed out to the writer by Mr. R. E. Wilson that a difficulty arises in the application of the kinetic theory to the dissociation of a substance such as calcium carbonate.

We may assume that in the equilibrium between calcium carbonate, calcium oxide and carbon dioxide two opposing reactions are taking place at equal rates. Off-hand, the most natural assumption in regard to these reactions would seem to be that the rate at which carbon dioxide is converted into carbonate is proportional to the pressure  $p$  of carbon dioxide and to the fraction  $\theta_1$  of the surface which is covered by CaO. On the other hand the rate of dissociation of the carbonate would be proportional to the fraction  $\theta_2$  of the surface covered by  $\text{CaCO}_3$ .

If we equate these two rates we obtain for equilibrium

$$p\theta_1 = K\theta_2 \quad (12)$$

where  $K$  is the equilibrium constant. This equation indicates that the pressure of the  $\text{CO}_2$  should depend on the ratio between  $\theta_2$  and  $\theta_1$ ; in other words it should depend on the relative proportions of the CaO and  $\text{CaCO}_3$ . This is contrary to fact. Evidently, therefore, we have made wrong assumptions regarding the mechanism of the reaction.

If we examine Equation 12 in the light of the Phase Rule we see that it would fit the facts well if there were a single solid phase of variable composition instead of two phases of constant composition. It would apply for instance to the dissociation of ferric oxide recently studied by Sosman and Hostetter<sup>2</sup> who found a "continuous series of solid solutions from  $\text{Fe}_2\text{O}_3$  over to a point very near  $\text{Fe}_3\text{O}_4$  if not over the entire range to  $\text{Fe}_3\text{O}_4$ ."

Furthermore, when we analyze the assumptions made in the derivation of Equation 12 we readily see that they imply a solid solution phase. Thus if the rate of dissociation of  $\text{CaCO}_3$  were proportional to the fraction of the surface covered by  $\text{CaCO}_3$  it is evident that the surface would soon

<sup>1</sup> See papers by Abegg and Johnson, *Z. physik. Chem.*, 61, 455 and 457 (1908); Scheffer, *Proc. Akad. Wetenschappen Amsterdam*, 18, 446 (1915).

<sup>2</sup> *THIS JOURNAL*, 38, 807 (1916).

consist of  $\text{CaO}$  and  $\text{CaCO}_3$  molecules distributed haphazard over the surface. This is exactly the kind of surface we should expect a solid solution to have.

The assumptions made above evidently are not consistent with the existence of separate phases of constant composition.

The Phase Rule, however, indicates that in the dissociation of calcium carbonate two solid phases,  $\text{CaO}$  and  $\text{CaCO}_3$ , are present together. In order that  $\text{CaCO}_3$  may dissociate and form a phase of  $\text{CaO}$  (instead of a solid solution) it is *necessary that the reaction shall occur only at the boundary between two phases.*

Now the  $\text{CaO}$  phase is generally so porous that  $\text{CO}_2$  readily diffuses through it. We are then forced to conclude that the  $\text{CO}_2$  in passing through the  $\text{CaO}$  does not react until it reaches the boundary of the  $\text{CaCO}_3$  phase. In a sense, therefore, calcium carbonate must be looked upon as a catalyst for the reaction between calcium oxide and carbon dioxide.

From the kinetic point of view this must mean that carbon dioxide molecules are only absorbed to form calcium carbonate when by so doing they form a continuation of a calcium carbonate crystal already present.

It will be remembered that in the calcite crystal each carbon atom is surrounded by three systematically placed oxygen atoms. By examining a model of such a crystal it is readily seen that in the cleavage surfaces two of the oxygen atoms are probably close to the surface, while the third lies well under the surface. In the readjustment of the positions of the surface atoms which must occur when a cleavage surface is found, the atoms must tend to assume positions in which the forces between the atoms are balanced against one another. Such an arrangement may have a considerable degree of stability.

If we imagine one of the carbon atoms, with the pair of oxygen atoms adjacent to it, to be removed from the surface, the symmetry of the arrangement of the surface atoms will be destroyed. This disturbance of the surface will certainly have an effect on the balance of forces holding the adjacent atoms. These atoms, therefore, will shift their positions. The neighboring carbon atoms (with their oxygen atoms) will then be held to the surface by a force which is *different* from that obtaining before the first  $\text{CO}_2$  was removed.

Now if this force has been *strengthened*, then the adjacent molecules of  $\text{CO}_2$  will be less likely to leave than others further from the disturbed region. Therefore, if the crystal is sufficiently heated,  $\text{CO}_2$  would leave from all portions of the surface and a *solid solution* of  $\text{CaO}$  in  $\text{CaCO}_3$  would be found. On the other hand if the removal of one  $\text{CO}_2$  molecule sufficiently *weakens* the force by which the adjacent ones are held, then the  $\text{CO}_2$  molecules will leave the surface only from positions adjacent to those from which they have already left. Under these conditions a



separate phase of CaO would grow, starting from the point (nucleus) where the first CO<sub>2</sub> molecule left the surface.

We may therefore conclude, in the case of the dissociation of calcium carbonate that the removal of a CO<sub>2</sub> molecule causes a weakening of the forces by which adjacent molecules are held, whereas in the case of the dissociation of ferric oxide the removal of an oxygen atom does not weaken the forces holding the adjacent oxygen atoms.

When a molecule of CO<sub>2</sub> strikes a surface of the CaO phase it presumably condenses and may be held to the surface by forces no different in kind from those holding the calcite crystal together. However, if the removal of one CO<sub>2</sub> molecule from a surface weakens the forces by which adjacent ones are held, it is probable that the forces acting on a single CO<sub>2</sub> molecule in the midst of a surface of CaO would be extremely weak. Therefore, the CO<sub>2</sub> molecule would remain on such a surface such a short time, that the total number present in the CaO phase would not be of importance.

If, on the other hand, the forces holding the CO<sub>2</sub> molecule in the CaO phase were at all comparable with those acting at the boundary of the CaCO<sub>3</sub> phase, then we should have a variable phase, consisting of a solid solution of CO<sub>2</sub> in CaO, together with a constant phase of CaCO<sub>3</sub>.

It is readily seen that the mechanism we have assumed, is capable of accounting for the different kinds of heterogeneous equilibria covered by the Phase Rule.

When there are two solid phases of constant composition and a gas, as in the dissociation of calcium carbonate, it follows directly from this mechanism that the pressure of the gas is dependent only on the temperature and not on the relative proportions of the phases.

Thus the rate at which CaCO<sub>3</sub> dissociates is proportional to the number of *CaCO<sub>3</sub> groups adjacent to empty spaces*, while the rate at which CaCO<sub>3</sub> is formed is proportional to the pressure of CO<sub>2</sub> and to the number of *empty spaces adjacent to CaCO<sub>3</sub> groups*. Therefore, the pressure must be constant at a given temperature.<sup>1</sup>

This theory of the mechanism of heterogeneous equilibria appears to be particularly useful in accounting for various conditions not usually predicted by the Phase Rule.

Faraday<sup>2</sup> noted a case that fully justifies the assumption that in some

<sup>1</sup> Since developing the above theory of the mechanism of such heterogeneous equilibria I have found that this subject has been treated by A. Thiel (*Sitzber. d. Ges. zur Beforderung d. gesamt. Naturwiss. in Marburg* (1913); *C. A.*, 8, 2284 (1914)). Thiel accepts as an axiom the relation given by Equation 12 and hence concludes that  $\theta_1/\theta_2$  is necessarily constant at a given temperature. This result is at complete variance with the theory given above, and, in the writer's opinion, is wholly unsupported by experimental evidence. In a subsequent paper the writer expects to discuss Thiel's theory in more detail.

<sup>2</sup> "Experimental Researches," page 109, Everyman's Library Edition.

equilibria the reaction can occur only when the surface has been disturbed. To quote from Faraday: "As a curious illustration of the influences of mechanical forces over chemical affinity, I will quote the refusal of certain substances to effloresce when their surfaces are perfect, which yield immediately upon the surface being broken. If crystals of carbonate of soda, or phosphate of soda, or sulfate of soda having no part of their surfaces broken, be preserved from external violence, they will not effloresce. I have thus retained crystals of carbonate of soda perfectly transparent and unchanged from September, 1827 to January, 1833; and crystals of sulfate of soda from May, 1832 to the present time, November, 1833. If any part of the surface were scratched or broken, then efflorescence began at that part, and covered the whole. The crystals were merely placed in evaporating basins and covered with paper."

It is well known that there is often great difficulty in removing the last traces of water of crystallization from a substance even when the hydrate gives a definite vapor pressure. According to the theory given above, the velocity of the dissociation is proportional to the area of the boundary between the phases. This boundary will usually have its maximum extent when both phases are present in more or less equivalent amounts. But the great difficulty in removing the last traces is undoubtedly due to the formation of solid solutions (adsorption!). Let us consider a crystalline substance AB which dissociates into a solid phase A and a gas B. The dissociation of AB and the recombination of A with B takes place most easily at the boundary between the phases AB and A. However, in general, we should expect that A and B also combine throughout the phase A, but that this compound is more unstable, and therefore dissociates at a higher rate. The rate at which A and B combine in this way in a unit volume of the phase A, will be proportional to the pressure  $p$ , while the rate at which it dissociates will be proportional to the concentration of B in A. By equating the two rates we see that the concentration of B in A should be proportional to the pressure of B.

There will, therefore, be the same kind of difficulty in removing the last trace of B from A as there is in producing a perfect vacuum.

The tendency of different substances to form these solid solutions will depend upon the extent to which the removal of one molecule of B from the phase AB affects the forces holding the adjacent molecules of B in AB.

It is a common experience that substances that are too thoroughly dehydrated are poor absorbers of moisture. A familiar example is overburnt lime or plaster of Paris. In some cases this phenomena may be due to a decrease in the porosity of the substance by sintering, but there is much evidence that this is not always the explanation.

According to the theory given above, the rate at which a partially dehydrated substance (which has a definite vapor pressure of moisture)

will absorb moisture, should be proportional to the extent of the boundary between the hydrated and dehydrated phases. According to this simple theory a thoroughly dehydrated substance should be incapable of absorbing any moisture. However, in general, there is no reason why vapor should not be slowly absorbed to from a solid solution even with a dehydrated substance. Gradually nuclei would develop in this solid solution and the hydrated phase would appear. The rate of absorption of moisture would then rapidly increase as the surface area of the hydrated phase grows.

### Adsorption of Gases by Solids.

Unless the molecules of a gas which may strike a solid surface *all* rebound elastically there will necessarily be a higher concentration of molecules of the gas in the surface layer of the solid than in the body of the gas. If any molecules impinging on the surface are condensed, a certain time interval must elapse before they can evaporate. This time lag will bring about the accumulation of molecules in the surface layer, and may thus be looked upon as the cause of adsorption.

In the condensation of a vapor we have seen that the collisions are wholly inelastic, so that every molecule striking the surface condenses.

The reasons that have led us to this conclusion apply with nearly equal weight to gas molecules of almost any kind striking any surface.<sup>1</sup>

Let  $\mu$  represent the number of gram molecules of gas striking each sq. cm. of surface per second. The quantity  $\mu$  can be readily calculated from the pressure by means of the following equation, derived from Equation 4:<sup>2</sup>

$$\mu = 43.75 \times 10^{-8} \frac{p}{\sqrt{MT}} \quad (13)$$

The rate at which gas condenses on the surface will then be  $\alpha\mu$ , where  $\alpha$  is a quantity usually very close to unity (never exceeding unity).

If the surface is that of a crystal, there will be a definite number of spaces,  $N_0$ , on each sq. cm. of surface capable of holding adsorbed gas molecules. A greater number of gas molecules can only be adsorbed by the formation of additional layers of molecules. The forces acting between two layers of gas molecules will usually be very much less than those

<sup>1</sup> There is good experimental evidence that this rule is not of universal application. When hydrogen molecules strike surfaces at room temperature apparently something like 80% are diffusely reflected. This probably represents nearly the extreme case. However, even if 80% of the molecules are reflected, the adsorption of the gas on a surface is only 5 times less than it would be if none were reflected. Therefore every gas must be adsorbed to some extent on every surface. The evidence in regard to the reflection and condensation of gas molecules on surfaces is given in detail in a recent article (*Phys. Rev.*, 8, 149 (1916)).

<sup>2</sup> The nomenclature used here is the same as that employed in a recent paper on the dissociation of hydrogen (*THIS JOURNAL*, 38, 1148 (1916)).

between the crystal surface and the first layer of molecules. The rate of evaporation in the second layer will, therefore, generally be so much more rapid than in the first, that the number of molecules in the second layer will be negligible.<sup>1</sup> When a gas molecule strikes a portion of the surface already covered, it thus evaporates so quickly that in effect it is equivalent to a reflection. Therefore, the rate of condensation of the gas on the crystal surface is  $\alpha\theta\mu$  where  $\theta$  represents the fraction of the surface which is bare. Similarly the rate of evaporation of the molecules from the surface is equal to  $\nu_1\theta_1$  where  $\nu_1$  is the rate at which the gas would evaporate if the surface were completely covered and  $\theta_1$  is the fraction actually covered by the adsorbed molecules. When a gas is in equilibrium with a solid surface these two rates must be equal so we have

$$\alpha\theta\mu = \nu_1\theta_1. \quad (14)$$

Furthermore

$$\theta + \theta_1 = 1. \quad (15)$$

Whence

$$\theta_1 = \frac{\alpha\mu}{\nu_1 + \alpha\mu}. \quad (16)$$

The quantity  $\theta_1$  is a measure of the amount of gas adsorbed. It should be noted that for low gas pressures the amount of adsorbed gas is proportional to the pressure, but as the pressure increases  $\theta_1$  increases more slowly and finally the surface becomes saturated ( $\theta_1 = 1$ ). These relations are in good qualitative agreement with known facts.<sup>2</sup>

Equation 16 indicates that at low temperatures (small value of  $\nu_1$ ) the amount of adsorption should be large and nearly independent of the pressure, while at higher temperatures (large value of  $\nu_1$ ) the amount of adsorption should be small, and should be proportional to the pressure even at high pressures. These deductions also are in qualitative accord with experimental facts.

From Equation 16 we see that the tendency of a gas to be adsorbed on a surface is determined by  $\nu_1$ , the rate of evaporation from the surface. This quantity in turn depends on the magnitude of the forces acting between the atoms of the crystal and those of the adsorbed substance.

<sup>1</sup> The detailed development of this theory of adsorption, taking into account the evaporation from each of the layers and other complicating factors, will be published as Part II of the paper in the *Phys. Rev.* References to previous literature on the subject will be given at that time. The present paper deals principally with the chemical aspects of the theory.

<sup>2</sup> Equation 16 gives the amount of adsorption on a plane crystal surface. No reliable quantitative experimental data seem to be available for the adsorption of gases on such surfaces. The writer is, therefore, undertaking measurements of this kind at present and will report the results at a later date. The theoretical reasons for believing that Equation 16 is not quantitatively applicable to adsorption by porous bodies such as charcoal will be discussed further on in this paper.

These forces will be of the same nature as those which hold solid bodies together. We may, therefore, profitably look upon them as chemical forces and apply our knowledge of the chemical properties in studying the phenomena of adsorption.

With a gas such as nitrogen, in which the atoms are mutually very thoroughly saturated, we know that there is only a weak field of force around the molecules. When a nitrogen molecule strikes a surface the forces holding it are only those due to weak secondary valence. It is to be expected, however, in general, that the forces by which molecules or atoms may be held on a surface, should show, for different substances, as great a range of intensity as is observed in the case of the forces acting inside of solid bodies.

Solid nitrogen is held together by comparatively weak forces, while the forces in solid carbon or tungsten are among the most powerful known. In the case of adsorbed films the magnitude of the forces should vary all the way from the weak forces observed with adsorbed nitrogen (or better helium) up to forces which are as intense as those holding together the atoms of the most stable chemical compounds. Just as we find either secondary or primary valences active between atoms in solids, so should we expect both kinds of valence to take part in the formation of adsorbed films. When we thus speak of adsorption as a chemical phenomena it should be remembered that we must also regard evaporation and condensation in general as chemical phenomena. The point to be emphasized is, that there is no real distinction between these so-called physical phenomena, and true chemical phenomena except that in general the "physical" phenomena depend on secondary valence rather than primary. Since, however, chemical phenomena involve secondary valence as well as primary, it seems best to classify all such phenomena as chemical. By so doing we do not in any way fail to recognize the close relationship between evaporation, condensation and the adsorption of the relatively inert gases.

This chemical theory of adsorption has received striking confirmation by many experiments in this laboratory.

**Experimental Evidence that Adsorption is a Chemical Phenomena.**—It has been found<sup>1</sup> that atomic hydrogen, produced by heating a metallic wire in dry hydrogen at very low pressures, has a remarkable tendency to be adsorbed on surfaces. According to the usual "physical" theory of adsorption by which the adsorbed film is assumed to be a layer of highly compressed gas we should expect that a gas of such low density as atomic hydrogen would be only slightly adsorbed. Furthermore, we should expect that an adsorption film in high vacuum would very rapidly reach equilibrium with its surroundings.

<sup>1</sup> Langmuir, *THIS JOURNAL*, 34, 1310 (1912).

The experiments showed, however, that even in the highest vacuum quantities of hydrogen as large as 0.01 to 0.03 cubic mm. (at atmospheric pressure) per sq. cm. could be adsorbed on cold glass, and that this adsorbed film was remarkably stable, being able to remain unchanged on the surface for several days. To account for these adsorption phenomena it was suggested in 1912<sup>1</sup> that "perhaps the unsaturated chemical affinity of the atomic hydrogen gives it unusual tendencies to be adsorbed on surfaces." It was observed that the amount of atomic hydrogen which could accumulate on a given surface was strictly limited and it was shown that this was not due to a balance between the rate at which atomic hydrogen spontaneously escaped from the surface, and the rate at which it was deposited. On the contrary, it was shown that the amount was limited because, after a certain amount of atomic hydrogen was present on the surface, fresh atoms of hydrogen striking the surface combined with those already present, and thus removed them.

It is interesting to compare the amount of atomic hydrogen adsorbed on the glass with the amount necessary to form a layer one atom deep. If we take the diameter of the hydrogen atom to be the same as that of the molecule, namely about  $2.5 \times 10^{-8}$  cm., we may conclude that the number of hydrogen atoms per sq. cm. needed to form a layer one atom deep is about  $1.6 \times 10^{15}$ . This corresponds to 0.032 cubic mm. of molecular hydrogen at 20° and one megabar pressure. The maximum amounts of atomic hydrogen which were found adsorbed on glass surfaces were of this same order of magnitude (0.01 to 0.03 cubic mm. per sq. cm.).

In a subsequent paper<sup>2</sup> it was shown that atomic hydrogen could diffuse several feet through glass tubes at room temperature, but could not pass even through a short tube cooled in liquid air. This may be taken as evidence that practically all hydrogen atoms striking a cold glass surface condense. With the glass cooled by liquid air these atoms do not evaporate at a perceptible rate, but from glass at room temperature they evaporate sufficiently rapidly to permit the passage of the atomic hydrogen through a long tube.

The experiments with atomic hydrogen thus furnish evidence that

1. The adsorption is determined by chemical affinity.
2. The adsorbed layer does not exceed one atom in thickness.
3. Hydrogen atoms striking glass surfaces are not reflected.

Similar evidence has been obtained from experiments with tungsten filaments in oxygen at low pressures. It was shown<sup>3</sup> that 15% of all oxygen molecules striking a tungsten filament at 2770° K. react with it to form  $\text{WO}_3$ . More recent experiments (as yet unpublished) have shown that this

<sup>1</sup> *Loc. cit.*, p. 1313.

<sup>2</sup> Freeman, *THIS JOURNAL*, 35, 927 (1913).

<sup>3</sup> Langmuir, *Ibid.*, 35, 105 (1913).

coefficient continues to increase at higher temperatures, so that at  $3300^{\circ}$  K. about 50% of all the oxygen molecules which strike the filament react with it to form  $\text{WO}_3$ . Since there are three atoms of oxygen in  $\text{WO}_3$ , and only two in the oxygen molecule, it is evident that *at least* one-half of the tungsten surface even at  $3300^{\circ}$  K. must be covered with oxygen in some form. When we consider that the pressure of oxygen in these experiments was usually not over 5 bars we realize the extraordinary stability of the film, and are thus led to believe that the oxygen atoms are held by chemical forces to the tungsten atoms which form the lattice structure of the tungsten crystals.

It is very evident that the adsorbed film does not consist of tungsten oxide  $\text{WO}_3$ , since this substance distills very rapidly from the filament even at temperatures as low as  $1200^{\circ}$  K. The film has no perceptible effect on the optical properties of the tungsten surface, since low pressures of oxygen do not cause any perceptible change in the characteristics (volts, amperes, candle-power) of the tungsten filament.

The existence of this oxygen layer on a tungsten filament in oxygen at low pressure, shows itself in many other ways. Thus a pressure of 0.001 bar of oxygen lowers the electron emission from a tungsten filament at  $1800^{\circ}$  to a very small fraction of its normal value. Even more striking evidence has been recently found in connection with experiments (as yet unpublished) with tungsten filaments in mixtures of various gases at low pressures. It is found that a tungsten filament at  $1500^{\circ}$  K. in a mixture of oxygen and hydrogen reacts with the oxygen exactly as if no hydrogen were present. While this oxidation of the tungsten is going on, none of the hydrogen reacts with the oxygen, and the hydrogen does not reduce any of the tungsten oxide<sup>1</sup> formed, nor is any atomic hydrogen produced. However, after all of the oxygen has been used up (partial pressure reduced to less than 0.01 bar) the hydrogen *suddenly* begins to disappear by being dissociated into atoms which then react with the  $\text{WO}_3$  previously deposited on the bulb.

Simultaneous measurements of the electron emission show that this emission increases suddenly at the same moment at which the hydrogen begins to disappear.

This experiment proves:

1. That in presence of even 0.01 bar of oxygen the surface of the tungsten at  $1500^{\circ}$  K. is practically completely covered with oxygen.
2. That this layer of oxygen will not react with hydrogen even at  $1500^{\circ}$  K.
3. That such a layer of oxygen prevents the formation of atomic hydrogen.

<sup>1</sup> This is especially remarkable since  $\text{WO}_3$  is readily reduced by hydrogen at atmospheric pressure at temperatures as low as  $500^{\circ}$ .

4. That the decrease in electron emission produced by oxygen is due to the same cause as that which prevents the dissociation of hydrogen.

It is very evident from this work that the oxygen layer has totally different properties from those we should expect, either with a layer of oxide, or a film of highly compressed gas. The facts are in good accord, however, with the theory that the oxygen atoms are chemically combined with the tungsten atoms. From this viewpoint the two primary valences of the oxygen are turned downwards, and are saturated by the tungsten, so that a hydrogen molecule striking the surface cannot react with the oxygen, and cannot come in contact with the tungsten. The hexavalent tungsten atoms, on the other hand, are not saturated by the oxygen, so that they are held firmly to the underlying layer of tungsten atoms. Only when the tungsten atoms on the surface become saturated by taking up two other oxygen atoms do they cease to be held to the other tungsten atoms, and thus evaporate off as  $\text{WO}_3$ .<sup>1</sup>

The stability of the oxygen layer is due to the strength of the chemical union between oxygen and tungsten atoms, which results in a very slow rate of evaporation of the oxygen atoms from the surface.

The action of oxygen in preventing the dissociation of hydrogen by a heated tungsten filament is clearly that of a *catalytic poison*. It has been shown previously<sup>2</sup> that the dissociation of hydrogen takes place only among hydrogen molecules adsorbed on the surface of the tungsten. The only way in which oxygen can prevent such action in a high vacuum is by the actual presence of oxygen atoms on the surface. Since the dissociation at  $1500^\circ \text{K}$ . is entirely prevented by the oxygen, and since the range of atomic and molecular forces does not exceed the dimensions of the atoms, it must follow that much more than half the surface must be covered by oxygen atoms or molecules. For if the surface were only half covered, then, according to probability laws, uncovered areas several times as large as the diameters of atoms would not be of rare occurrence, and on these areas dissociation could occur.

Now if this adsorbed oxygen were present on the surface as a layer of compressed gas<sup>3</sup> it would be inconceivable that it should not react at all

<sup>1</sup> The fact that the tungsten atoms leave the surface only after they have been completely saturated chemically seems to be an example of a general tendency. Thus when tungsten is heated in chlorine at very low pressures the hexachloride  $\text{WCl}_6$  only is formed, although several stable lower chlorides of tungsten exist. When Pt is heated at high temperatures in oxygen at moderate pressures the oxide  $\text{PtO}_2$  distills from the surface, while an osmium filament in oxygen at low pressures gives  $\text{OsO}_4$ . Molybdenum in oxygen gives only  $\text{MoO}_3$ .

<sup>2</sup> THIS JOURNAL, 38, 1145 (1916).

<sup>3</sup> The commonly accepted theories of adsorption are based upon the assumption that there is a transition layer (van der Waals) in which the density varies gradually from that of the solid or liquid phase to that of the surrounding gas. Eucken (*Verh. deut. physik. Ges.*, 16, 345 (1914)), for example, considers that this transition layer is a



with hydrogen at a temperature of  $1500^{\circ}$  K. Even if we should regard the adsorbed layer as consisting of adsorbed tungsten oxide we would be no nearer an explanation, for tungsten oxide is readily reduced to metallic tungsten by hydrogen at temperatures of  $500^{\circ}$ . We should have to say, with Bancroft, that the oxide is stabilized by adsorption. But, of course, this is a mere description and not an explanation of the phenomena.

It is very clear that the oxygen by being adsorbed has undergone a complete change in chemical properties and it is certainly not logical to consider that this has been brought about by a mere compression of the gas into a surface layer.

If, however, we assume that the oxygen atoms are chemically combined to the mass of the tungsten filament and form a *continuous* surface layer, all of the observed facts are readily accounted for. The oxygen atoms are saturated chemically by the tungsten (primary valence) and the field of force holding the oxygen atoms lies wholly below the surface where hydrogen molecules cannot reach it. When the pressure of oxygen falls so low that the supply of this gas at the surface is not sufficient to make up for the loss by evaporation, then gaps are formed in the continuous covering and the hydrogen is then able to make a *flank attack* on the oxygen. In this way the oxygen covering is *suddenly* removed when the pressure of oxygen falls below a certain critical value, and the dissociation of hydrogen, therefore, begins at once.<sup>1</sup>

The resemblance between the action of oxygen on a tungsten filament and the phenomena of electrochemical passivity is very striking, so much so, in fact, that the mechanism of passivity is probably similar to that of the effects described above.<sup>2</sup>

According to this theory the effect of oxygen in poisoning the catalytic activity of tungsten is due to the formation of an exceptionally stable film of oxygen which is combined with and completely covers the surface of the tungsten.

The effects of the poisoning of tungsten by oxygen are also to be seen in many other reactions in gases at low pressures (10–100 bars), of which the following may be briefly mentioned.

sort of miniature atmosphere. Bakker (*Z. physik. Chem.*, 89, 1 (1915)) has a similar theory to account for surface-tension phenomena.

<sup>1</sup> The strongest evidence of the correctness of this theory is obtained from experiments at higher filament temperatures than  $1700^{\circ}$  K. The hydrogen and oxygen then begin to react with each other on the surface of the filament. The further development of this theory is reserved for a future paper, in which the detailed experimental results will be published.

<sup>2</sup> An outline of this theory of passivity together with a brief description of the experiments with mixtures of oxygen and hydrogen in contact with a hot tungsten filament was given by the writer in a discussion of Bennett and Burnham's paper on Passivity, at the Washington meeting of the American Electrochemical Society, April 28, 1916. This discussion has been published in Vol. 29 of the Transactions.

When a tungsten filament is heated in a mixture of carbon monoxide and oxygen, tungsten is oxidized just as if no carbon monoxide were present. None of the CO reacts with the oxygen even when the filament is heated as high as  $2800^{\circ}\text{K}$ ., whereas hydrogen begins to react with oxygen in contact with a tungsten filament when the temperature exceeds about  $1700^{\circ}\text{K}$ . Evidently CO will not combine with oxygen adsorbed on a heated tungsten filament even if it has a chance to make a "flank attack."

Mixtures of methane and oxygen at low pressures do not react with one another in contact with tungsten at  $1500^{\circ}$  or even  $1800^{\circ}\text{K}$ . but the tungsten is oxidized to form  $\text{WO}_3$  as in the previous cases. In absence of oxygen, methane is gradually decomposed, setting free hydrogen, while the carbon is taken up by the tungsten filament, forming a solid solution. Even this action is prevented by the presence of traces of oxygen. On the other hand, if the filament is first heated in methane, so that it has taken up carbon, and then oxygen is admitted, the oxygen reacts with the carbon in the filament forming CO, and until all the carbon from the surface layers has been removed, the oxygen does not react with the tungsten. This proves that when carbon is taken up by tungsten some of the carbon remains as an adsorbed layer of carbon atoms.

Dry ammonia at low pressures is decomposed fairly rapidly by a tungsten filament at  $1000^{\circ}\text{K}$ . but with a platinum filament the same rate of decomposition only occurs at a temperature of nearly  $1400^{\circ}\text{K}$ . In the presence of small amounts of oxygen, however, the tungsten filament fails to decompose ammonia even at  $1200^{\circ}\text{K}$ . At  $1300^{\circ}\text{K}$ . the tungsten oxidizes just as if the ammonia were absent, the oxide  $\text{WO}_3$  distilling to the bulb. Some of the ammonia seems to react with the oxygen, but with an excess of ammonia this reaction goes on slowly until the oxygen is consumed, and the remainder of the ammonia is then rapidly dissociated. The oxygen thus poisons the tungsten even in the case of the simple dissociation of ammonia by heat. In contact with platinum, however, ammonia and oxygen react together at a temperature well below  $1000^{\circ}\text{K}$ . Particularly interesting effects are observed when a tungsten or platinum filament is heated in mixtures of cyanogen and oxygen. In this case, with a filament at  $1500^{\circ}\text{K}$ . the oxidation of the tungsten is largely prevented until the cyanogen has been slowly oxidized to carbon monoxide and nitrogen. If there is an excess of oxygen this then reacts with the tungsten when the supply of cyanogen is used up. Any excess of cyanogen is decomposed by the filament giving nitrogen, the carbon being taken up by the filament. Thus cyanogen may be looked upon as having a stronger poisoning effect on tungsten than oxygen has.

It is well known that cyanogen poisons the catalytic activity of platinum. Experiments at low pressures furnish a remarkable demonstration of this fact.

A platinum filament at a temperature of  $600^{\circ}$  K. causes carbon monoxide and oxygen to combine rapidly, the carbon monoxide, however, itself, acting as a catalytic poison.<sup>1</sup> At higher temperatures ( $900^{\circ}$  K.) the poisoning effect of the carbon monoxide disappears and the velocity of the reaction becomes enormously high, being then limited only by the rate at which the two gases can come into contact with the platinum surface, according to Equation 4.

But if a trace of cyanogen is added to the mixture of oxygen and carbon monoxide (at a pressure of 10 bars) the catalytic action of the platinum disappears completely even at  $900^{\circ}$  K. By raising the temperature to about  $1000^{\circ}$  the cyanogen reacts with the oxygen to form nitrogen and carbon monoxide. As soon as the cyanogen is all oxidized the catalytic activity of the platinum is restored and the oxygen and carbon monoxide then react rapidly to form carbon dioxide.

The catalytic effect of platinum on the reaction between oxygen and hydrogen is also poisoned by traces of cyanogen. If the temperature of the platinum is then raised, the cyanogen and hydrogen react together to form hydrocyanic acid.

The fact that these low pressures of cyanogen (or oxygen) can exert such a powerful poisoning effect is proof that adsorbed films of great stability are formed, in other words, films in which the rate of evaporation of the adsorbed molecules is remarkably low. The effect of these poisons is thus merely to cover up the active surface.

The property of cyanogen in poisoning metallic catalyzers is thus closely related to the chemical facts that cyanogen forms very stable compounds with metals, and shows an unusual tendency to form complex salts. The cyanogen radical is one in which both the primary and the secondary valences are strongly developed.

Water vapor has the same effect in poisoning the catalytic activity of tungsten that oxygen has. A partial pressure of 0.4 bar of water vapor (vapor pressure of water at  $-78^{\circ}$ ) is sufficient to prevent the dissociation of hydrogen by a tungsten filament at  $1500^{\circ}$  K.

It is a remarkable fact that carbon dioxide, although it oxidizes a tungsten filament to form  $WO_3$ , does not have any effect upon the rate of dissociation of hydrogen. We must, therefore, conclude in this case that only a very small fraction of the tungsten surface is covered by adsorbed oxygen. This conclusion is also supported by the fact that the rate of oxidation of tungsten by carbon dioxide is extremely slow compared to the rate of oxidation by oxygen. We shall see that further evidence of the same kind is furnished by measurements of the electron emission. However, since the oxygen from at least two molecules of carbon dioxide

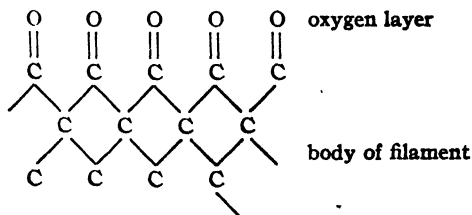
<sup>1</sup> Langmuir, *THIS JOURNAL*, 37, 1163 (1915).

is needed to produce a molecule of  $\text{WO}_3$ , it is certain that the reaction depends upon the presence of adsorbed oxygen partially covering the surface. The velocity of the reaction between carbon dioxide and tungsten seems to be approximately proportional to the square root of the pressure of  $\text{CO}_2$  and inversely proportional to the pressure of carbon monoxide.

When molybdenum filaments are heated in oxygen at low pressures the filaments become tarnished unless the temperature is maintained above  $1500^\circ \text{K}$ . Above this temperature the surface of the filament remains apparently clean, and the oxide formed,  $\text{MoO}_3$ , distills to the bulb. With tungsten, notwithstanding the fact that  $\text{WO}_3$  is much less volatile than  $\text{MoO}_3$ , it is only necessary to keep the temperature above about  $1250^\circ$  in order to have a clean surface.

Although oxygen is clearly adsorbed on molybdenum, it appears that the stability of the film is much less than that of the corresponding film on tungsten. This is shown not only by the electron emission (see below), but by the comparatively small effect of oxygen in poisoning the catalytic activity of molybdenum. Thus when molybdenum is heated to a temperature between  $1500$  and  $1800^\circ \text{K}$ . in a mixture of oxygen and hydrogen, it is found that the hydrogen disappears slowly until the oxygen is all used up, by reacting with the molybdenum. After that the rate of disappearance of the hydrogen is much greater. The fact that a part of the hydrogen disappears before the oxygen is consumed indicates that the poisoning effect of the oxygen is not complete.

Experiments with carbon filaments in oxygen, and in carbon monoxide or dioxide<sup>1</sup> have shown that oxygen acts as a catalytic poison, on the reaction between oxygen and carbon, and on that between carbon dioxide and carbon. It was also proved that this poisoning effect is due to a remarkably stable film of adsorbed oxygen, so stable in fact that the filament must be heated in a good vacuum for nearly half an hour at  $2300^\circ \text{K}$ . in order to distill it off. In this case there is very clear evidence that this film consists of oxygen atoms chemically combined by primary valences to the carbon atoms forming the body of the filament, according to the formula



A very peculiar case of adsorption occurs when a tungsten filament

<sup>1</sup> THIS JOURNAL, 37, 1154 (1915).

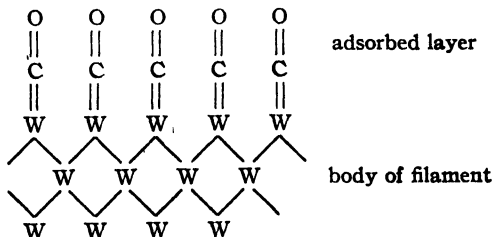
is heated to about  $2700^{\circ}$  K. in a low pressure of carbon monoxide contained in a bulb cooled by liquid air.<sup>1</sup>

With the bulb at this temperature the tungsten filament is attacked by the CO and a very stable adsorbed film is formed on the filament. This distills off at a constant rate (independent of the pressure of CO) taking the tungsten with it as a compound of the composition WCO. The most remarkable fact is that when the temperature of the bulb is raised to  $20^{\circ}$  or above, the CO no longer attacks the tungsten of the filament, but combines only with the tungsten which evaporates from the filament, still forming the compound WCO.

Before attempting to look for the probable mechanism of this action let us consider one more case of adsorption: that of nitrogen by *molybdenum vapor*. When a molybdenum filament is heated to  $2200^{\circ}$  K. in nitrogen contained in a bulb cooled in liquid air, nearly every molybdenum atom evaporating from the filament combines with the *first* nitrogen molecule which it strikes to form a compound  $\text{MoN}_2$  (stable at  $360^{\circ}$  in a vacuum). When the bulb is at room temperature the molybdenum atoms still combine with the first nitrogen molecule they strike, but most of the molecules thus formed are so unstable that they decompose when they strike the bulb, giving nitrogen and a spongy molybdenum deposit.

Thus when the nitrogen is at low temperature the compound appears to be  $\text{MoN}_2$  in which the atoms are held by primary valence, while the compound formed with the nitrogen at higher temperatures is  $\text{Mo} : \text{N}_2$ , in which the nitrogen and molybdenum are held by secondary valence. This seems then to be a kind of adsorption of one gas by another.

A somewhat similar explanation seems necessary for the reaction between tungsten and carbon monoxide. Thus when carbon monoxide molecules of low velocity and low internal energy (low temperature) strike the surface of the filament they combine with it by primary valences to form a stable structure, probably as follows:



The strength of the union between the oxygen and carbon, and between the tungsten and carbon, is so great, that the whole group WCO distills off as a single molecule. The fact that the tungsten is partially saturated

<sup>1</sup> A brief preliminary account of these experiments was published in *THIS JOURNAL*, 37, 1160 (1915). A more detailed paper will be presented later.

by the carbon should make this group somewhat more volatile than the tungsten itself. As a matter of fact the rate of evaporation of the WCO from the surface is only about five times greater than that of tungsten.

When the temperature of the bulb is higher, so that the CO molecules possess more internal energy (and a higher velocity) the CO is incapable of combining with the solid tungsten in the above manner. We must still assume that nearly every CO molecule which strikes the filament condenses on it, but that the union in this case is by secondary valence, so that the molecule almost immediately distills off again.

A more thorough study of this reaction may throw some light on the paradox that the residual valence of CO is small, although this substance contains a divalent carbon atom.

### **The Effect of Gases on the Electron Emission from Heated Metals as Evidence of the Presence of Stable Adsorbed Films.**

The effect of adsorbed films of the thickness of a single molecule on the electron emission from heated tungsten filaments was described by the writer in 1913.<sup>1</sup> A little later<sup>2</sup> the following theory of the effect was proposed. "The decrease in the electron emission from a hot cathode caused by certain gases is due to the formation of a film on the surface of the cathode. Whether this film consists of adsorbed gas, or of a chemical compound of the gas with the cathode material, is not definitely established, but most of the evidence is in favor of the latter view. The amount by which the electron emission is affected depends on the *extent* to which the surface is covered. The film should be looked upon as consisting of a single layer of molecules, or at most, of a very few layers. The extent to which the surface of the cathode is covered by the film depends upon: (1) The rate of formation of the film. (2). The rate of destruction of the film," etc.

The more recent work on chemical reactions at low pressures, and further experiments on electron emission, have furnished abundant evidence of the correctness of the above viewpoint, and have fully verified the conclusion that the film is held to the surface by chemical forces.

In every case with tungsten, chemically inert gases have been found to be without effect on the electron emission, whereas nearly all gases that react with the tungsten lower the emission.

The decrease of the electron current produced by a gas is thus caused by the formation of an adsorbed film of great stability, which covers the surface. The evidence is very strong that the electron emission at a given temperature depends only on the nature of the layer of atoms forming the actual surface of the filament. Here again we have proof of the ab-

<sup>1</sup> Langmuir, *Phys. Rev.*, **2**, 450 (1913).

<sup>2</sup> *Physik. Z.*, **15**, 520 (1914).

sence of a transition layer in which the density varies gradually from that of the filament to that of the surrounding space.

The lowering of the electron emission of heated filaments by adsorbed films thus bears a close relationship to the effect of these films in poisoning the catalytic activity of the filament. Both effects are caused by a film of great stability which covers the surface. The following experimental evidence shows, in fact, that there is a remarkable parallelism between the electron emission and the catalytic activity of a filament.

As has already been pointed out, oxygen enormously lowers the electron emission from tungsten. This effect of oxygen is in accord with its action as a catalytic poison for tungsten. Thus in mixtures of oxygen and hydrogen the electron emission undergoes a sudden increase at the moment at which the hydrogen begins to dissociate (after the consumption of all the oxygen).

It might be thought that the electron emission itself would have an effect on the chemical reactions occurring on the surface of a heated filament. But experiment has never shown any such direct effect. Thus the rate at which oxygen, hydrogen, carbon dioxide, and other gases disappear in contact with heated tungsten are found to be entirely independent of the thermionic currents. The presence of a negatively charged electrode close to the heated filament causes all electrons emitted to be driven back into the filament, but this does not affect the rate of disappearance of the gases. In some cases, however, electric discharges do cause the clean-up of gases, but this effect is due to the bombardment of the filament by positive ions, and not to the electron emission.

Nitrogen does not normally attack a tungsten filament at any temperature, although it combines (to form  $WN_2$ ) with tungsten vapor as fast as this evaporates from the filament.<sup>1</sup> Similarly nitrogen has no effect on the electron emission from tungsten if low voltages are used in making the measurements of the thermionic current. But if voltages high enough to cause ionization of the nitrogen are employed, then the tungsten is attacked by the rapidly moving positive nitrogen ions, and simultaneously the electron emission is greatly decreased, indicating that a film of adsorbed nitrogen is formed. If the filament is now allowed to cool to room temperature and the remaining nitrogen is pumped out, and the filament is then heated again to the same temperature as before, it is found that the electron emission is at first the same as it was in the presence of the nitrogen, showing that the electron emission is determined not by the gas around the filament, but by the film adsorbed on it. Gradually the adsorbed film distills off, and the electron emission returns to its normal value.

By the study of such lag effects, the rate of evaporation and the rate of

<sup>1</sup> THIS JOURNAL, 35, 931 (1913).

formation of the adsorbed films can be measured with accuracy, and it has thus been proved that the fraction of the surface covered often depends upon a dynamic equilibrium.

The fact that the rate of evaporation of these films even at temperatures of  $1800^{\circ}$  K. is slow enough to measure proves that they are remarkably stable.

Extremely interesting phenomena are observed after a tungsten filament has been heated in  $\text{CH}_4$  or  $\text{C}_2\text{N}_2$ , or other gas which gives up carbon to the filament. The most minute trace of carbon,<sup>1</sup> in the surface of the filament cuts down the electron emission to about one-third of that of an uncontaminated filament. But a filament which has taken up carbon is no longer sensitive to the effect of bombardment by positive nitrogen ions. In other words nitrogen has no effect on the electron emission from such a filament even if high anode voltages are used. Still more remarkable is the fact that oxygen instead of lowering the electron emission of a carbon-containing filament gradually raises it. The carbon is then gradually oxidized and the electron emission returns to the value corresponding to pure tungsten. Then when the carbon has all been removed, the oxygen begins to attack the tungsten and the electron emission suddenly decreases to one per cent. or less of its former value. After the excess oxygen has been consumed it is found that the electron emission is again sensitive to the effect of bombardment by positive nitrogen ions, the thermionic current decreasing as the voltage is raised.

This experiment is an excellent demonstration of the closeness of the relationship between the electron emission and the chemical activity of the filament.

Another illustration is afforded by the fact that water-vapor, which reacts rapidly with tungsten, and poisons the tungsten surface, has as great an effect on the electron emission as oxygen, while carbon dioxide, which reacts slowly with tungsten, and is not a catalytic poison, has practically no effect on the electron emission.

So far we have considered the effects of gases on the electron emission from tungsten. Striking effects of another kind are obtained when the filament contains minute amounts of thorium.<sup>2</sup> If such a filament is heated in a very high vacuum to  $2900^{\circ}$  K. for a short time and the electron emission at  $1800^{\circ}$  K. is then measured, it is found that the emission is the same as that of pure tungsten. By now heating the filament a few minutes at a temperature between  $2000^{\circ}$  and  $2500^{\circ}$  K. (preferably  $2300^{\circ}$  K.),

<sup>1</sup> Probably just enough to form a layer one atom deep over the surface of the filament is sufficient.

<sup>2</sup> An account of these phenomena was given before the American Phys. Soc., Oct. 31, 1914 (*Phys. Rev.*, 4, 544 (1914)). A paragraph describing the effect was given in a paper before the American Electrochemical Soc. (see *Trans. Am. Electrochem. Soc.*, 29, 353 (1916)).



the electron emission at  $1800^{\circ}$  K. is found to have increased enormously (more than 10000 fold). By heating again to  $2900^{\circ}$  the emission returns to its normal value.

This effect is due to the formation of an adsorbed layer of thorium atoms on the surface of the filament. At  $2900^{\circ}$  K. the thorium, being more volatile than tungsten, distills off the surface and leaves pure tungsten. At  $2300^{\circ}$  K. however, the rate of distillation is not very marked, but the rate of diffusion of the thorium through the tungsten is sufficient to allow the accumulation of thorium atoms on the surface. At  $1800^{\circ}$  the rate of diffusion is negligible, so that if the thorium is distilled off a fresh supply does not diffuse to the surface.

The tendency of thorium to form an adsorbed film on tungsten is in accord with other properties of thorium. Gibb's has shown that any substance which lowers the surface energy tends to be adsorbed on the surface. The Eötvös-Ramsay-Shields relation indicates that the surface energy of a substance at temperatures low compared to its critical temperature, should be approximately proportional to  $T_c A^{-2/3}$  where  $T_c$  is the critical temperature and  $A$  is the atomic volume. Now the critical temperature of thorium must be lower than that of tungsten, since the vapor-pressure of thorium is considerably greater than that of tungsten. The atomic volume of thorium is about 21, while that of tungsten is 9.6. Thus both  $T_c$  and  $A$  differ, for these metals, in such a way as to make the surface energy of thorium less than that of tungsten. Therefore, according to Gibb's rule thorium should tend to be adsorbed on the surface of tungsten.

By a study of the rate of growth of the adsorbed film at  $2100^{\circ}$  K. and the rate of evaporation at  $2700^{\circ}$  K. it has been possible to prove that the film grows until it is one atom deep but does not grow beyond this.<sup>1</sup> The real evidence in favor of these conclusions, however, can only be given in connection with a full discussion of the detailed experimental results. It is intended to publish these before long.

When oxygen is brought into contact with a tungsten filament (at  $1900^{\circ}$  K.) coated with a layer of thorium atoms, the electron emission is suddenly decreased to a value far below that corresponding to pure tungsten. With tungsten the effect of oxygen in decreasing the emission disappears as soon as all the oxygen has been consumed. But with a thorium-coated filament the effect of oxygen is more permanent, so that the emission remains low even after all oxygen has been removed. Only by heating the filament to  $2900^{\circ}$  and following this by a treatment at  $2300^{\circ}$  can the

<sup>1</sup> That the layer is never more than one atom deep is readily proved by the fact that the activity of the film always begins to decrease *at once* at  $2700^{\circ}$  no matter how long it may have been previously heated at  $2300^{\circ}$  K.

activity be restored. This behavior is in accord with the known facts that thorium has an unusually strong affinity for oxygen.

In the case of this oxidized thorium-coated filament the adsorbed film evidently consists of a layer of thorium atoms covered by a layer of oxygen atoms. It should not be looked upon as a layer of adsorbed thorium oxide.

Interesting effects are observed if a small amount of methane is brought into contact with an oxidized thorium-coated tungsten filament at about  $1900^{\circ}$  K. The electron emission suddenly increases to that of pure thorium, and then as suddenly decreases to a value below that of pure tungsten. The methane reacts with the oxygen on the surface of the filament, forming carbon monoxide, which evaporates off, leaving the layer of thorium atoms. The excess of methane is then decomposed, and a layer of carbon atoms is formed on the surface of the filament, and covers the thorium atoms. The electron emission then becomes that of a carbon surface which is a little less than that of tungsten, notwithstanding the presence of thorium atoms just under the surface layer.

Kruger and Taegge<sup>1</sup> have recently studied the effect of catalytic poisons on the photoelectric activity of platinum, using ultraviolet light. They find that minute traces of  $H_2S$ ,  $HCN$  or  $CO$  very greatly decrease the photoelectric electron emission. The mechanism of this action is undoubtedly identical with that of the effect on the thermionic electron emission. Debye<sup>2</sup> and Richardson<sup>3</sup> have shown that there is a very close relationship between the photoelectric and thermionic electron emission.<sup>4</sup>

**Adsorption Phenomena at Higher Gas Pressures.**—The effect of poisons on the activity of catalyzers is essentially the same with gases at atmospheric pressure as at lower pressures. There is every reason for believing that the theory of adsorption outlined in the preceding pages is applicable to the adsorption of gas at atmospheric pressures. In the second part of this paper we shall see that a similar theory also applies to adsorption in surface layers of liquids.

As the pressure of a gas increases the amount adsorbed on a plane surface should gradually increase until the surface becomes completely covered by a layer one molecule (or atom) deep. The surface thus becomes *saturated*. This is in full accord with experimental facts.

In the case of the adsorption of vapors at such high pressures that they approach the state of saturated vapors, there will be a tendency for the adsorbed film to become several molecules deep.

<sup>1</sup> *Z. Electrochem.*, **21**, 562 (1915).

<sup>2</sup> *Ann. Phys.*, **33**, 441 (1910).

<sup>3</sup> *Phil. Mag.*, **23**, 266, 615 (1912); **24**, 570 (1912).

<sup>4</sup> For a review of the recent work on this subject and its relation to contact potentials see a paper by Langmuir, *Trans. Am. Electrochem. Soc.*, **29**, 341 (1916).

According to this theory it is very improbable that films more than one or two molecules deep would ever be held on a surface by adsorption, except with nearly saturated vapors. We must assume that after a layer two or three molecules deep is formed, the rate of evaporation of additional molecules would be nearly identical with that from the liquefied or solidified gas. If the vapor pressure were well below saturation, the rate at which such additional molecules would condense in the surface would be much less than the rate at which they would evaporate. The adsorbed film would thus grow thinner.

There is considerable experimental evidence that the amount of moisture taken up by glass surfaces is greatly in excess of the amount needed to form a layer one molecule deep.

When a 40-watt incandescent lamp bulb is heated to  $500^{\circ}$  for several hours (after having been exhausted and dried out at room temperature) it gives off about 0.45 cc. of water vapor, 0.030 cc. of carbon dioxide, and 0.005 cc. of nitrogen.<sup>1</sup> The internal surface of this bulb was about 200 sq. cm. The number of molecules of gas given off per sq. cm. was thus  $56 \times 10^{15}$  molecules of  $H_2O$ ;  $37 \times 10^{15}$  molecules of  $CO_2$  and  $0.6 \times 10^{15}$  molecules of  $N_2$ . If we calculate the number of molecules of each of the gases necessary to cover a sq. cm. one molecule deep (taking the molecules to be cubical in shape) we find  $1.0 \times 10^{15}$  for  $H_2O$ ;  $0.77 \times 10^{15}$  for  $CO_2$  and  $0.67 \times 10^{15}$  for  $N_2$ . Thus the quantities of gas obtained from this bulb correspond to: a layer of water 55 molecules deep, a layer of carbon dioxide 4.8 molecules deep and a layer of nitrogen 0.9 molecule deep.

The adsorption(?) of water vapor by pulverized synthetic quartz and anorthite has been studied by J. R. Katz.<sup>2</sup> The amount of water taken up reaches a fairly definite limit when the vapor pressure of the water is about 0.7 of the saturated vapor. The quantities of water adsorbed per sq. cm. of surface under these conditions were  $1.3 \times 10^{-6}$  grams for quartz and  $6.2 \times 10^{-6}$  grams for anorthite. These correspond to layers of water 43 and 205 molecules deep, respectively. Freundlich<sup>3</sup> reviews the literature on the thickness of adsorbed films, and comes to the conclusion that these films in general range from  $10^{-7}$  to  $10^{-6}$  cm. in thickness. Since the diameters of atoms and molecules usually lie between  $2 \times 10^{-8}$  and  $5 \times 10^{-8}$  cm., the adsorbed films, according to Freundlich, should be many molecules thick. The evidence on which this conclusion is based is very meagre, and for the most part is quite indirect. The best data referred to are probably those of Ihmori.<sup>4</sup> According to Freund-

<sup>1</sup> Langmuir, *Trans. Am. Inst. Elec. Eng.*, 32, 1921 (1913).

<sup>2</sup> *Proc. Amsterdam Acad.*, 15, 445 (1912).

<sup>3</sup> "Kapillarchemie," Leipzig (1909), p. 265.

<sup>4</sup> *Wied. Ann.*, 31, 1006 (1887).

lich, Ihmori "found with polished metals (brass, steel, etc.) thicknesses for the surface layer of water ranging between 3 and  $10 \times 10^{-7}$  cm.; and with quartz, an average thickness of  $22 \times 10^{-7}$  cm."

However, by referring to Ihmori's original article, it appears that this investigator found that the amount of "adsorbed" moisture increased greatly (about 10 fold) if the metal had previously been allowed to stand in the air for a few weeks. With carefully cleaned (polished or ignited) platinum he could not detect any adsorption whatever, that is, the adsorbed film in this case must have been less than  $2 \times 10^{-8}$  cm. thick. Ihmori says "the small amount of water adsorbed by the metals designated as 'polished' is, perhaps, due to the presence of a thin film of oxide."

In Ihmori's experiments the pressure of the water vapor was about 92% of that at saturation.

From the cases considered above it appears that certain surfaces adsorb moisture in quantities very large compared to that necessary to form a layer one molecule thick. There is no evidence, however, that in any of the cases studied the phenomena is a true adsorption.

The term adsorption should be restricted to gas taken up *on a surface* without any penetration of the gas molecules between the atoms or molecules of the solid surface. The theory of adsorption developed in this paper indicates that the amount thus truly adsorbed should never exceed a layer one or two molecules in thickness.

But there is no reason whatever why molecules of gas or vapor should not penetrate in between atoms of the surface and thus be absorbed. Dried jellies can absorb large quantities of moisture, and dehydrated salts usually absorb moisture even when no definite hydrates are formed (solid solutions).

The absorption of moisture by a surface of glass is to be looked upon as a process of solution of the water into the glass. Dried sodium silicate absorbs moisture in this way in very large quantities, and it is not at all surprising that this property should not be wholly lost, when lime and other oxides are fused with the alkali silicate. The whole behavior of glass surfaces in giving up their moisture confirms this theory that the moisture penetrates to a very considerable depth into the surface. The remarkable slowness with which the moisture is given up on heating, and the length of time needed for the reabsorption of the moisture indicate that we are not dealing with a true adsorption phenomena.

In the case of Katz's experiments with anorthite and quartz, there is probably also a penetration of the moisture into the crystal substance. It is, however, quite possible that what he measured was the moisture actually condensed as liquid in the fine capillary spaces between the grains of the extremely fine powder experimented with.

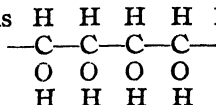
We may safely assume that water vapor would not penetrate at all into

a metal, so that a *clean* metal surface should never take up more moisture than enough to form a layer one molecule deep. This is in accord with Ihmori's results, since he could not detect absorption of moisture by platinum. The other metals used by Ihmori all oxidize in contact with air. The oxide layer formed is usually thick enough to see. When we consider that a film of metallic *tungsten* ten atoms thick only absorbs about 20% of the light striking it, it is evident that a film of *oxide* thick enough to see must be of very great thickness compared to that of a molecule. Furthermore, such a film must be quite porous, since the oxygen required for its growth must have diffused through it. It is, therefore, not remarkable that relatively large quantities of moisture are absorbed by such films.

**Adsorption by Porous Bodies.**—Nearly all quantitative measurements of the adsorption of gases by solids have been made with porous bodies such as charcoal. In these cases it is impossible to know definitely the area on which adsorption takes place.

It is often assumed that the surface of even a polished metal is porous to such an extent that its "true surface" is much greater than its apparent surface. As far as the writer knows, there is no experimental evidence to support any such assumption and theoretical considerations would make it seem extremely improbable. The strong surface forces (quite analogous to that in liquids) would tend to make the atoms in the surfaces of solids arrange themselves in such a way as to make the total surface a minimum. Therefore, in the absence of definite causes which produce a porous structure (such as those considered below), we should assume that the atoms of the surfaces are packed closely together and are arranged with considerable regularity. Thus a surface of glass should not be considered as porous, although it is capable of absorbing considerable quantities of moisture. The absorption is here a solution process, in other words, a chemical change by which the water molecules become combined (secondary valence) with the atoms of groups of atoms forming the glass. There is no more reason for assuming a porous structure than there is in the case of a liquid.

Truly porous bodies, such as charcoal, probably consist of atoms combined together in branching chains of great complexity. The fibers of cellulose from which charcoal is usually formed probably consist of practically endless groups of atoms



valences in the direction of their length and by secondary valence in the transverse directions. When the hydrogen and oxygen atoms are driven out by heat, the carbon atoms for the most part remain in their chains, but a certain number of cross linkages occur between these chains. The

porosity of the charcoal thus undoubtedly extends down to atomic dimensions. The unsaturated state of the remaining carbon atoms explains the practical impossibility of removing the last traces of oxygen and hydrogen from any form of amorphous carbon.

It is evident that with a structure of this kind, it is meaningless to talk about the surface on which adsorption can take place. With plane surfaces, we have seen that adsorption is usually limited to the formation of a layer one molecule deep, so that we can estimate the maximum adsorption from the extent of the surface. With charcoal, on the other hand, there is no definite surface which can be covered by a layer one molecule deep. Between the atoms of carbon, there must be spaces of all possible sizes and shapes, some just too small to hold a gas molecule, others big enough to hold one but not hold two, etc. There are some spaces in which a molecule would be closely surrounded by carbon atoms on nearly all sides, whereas in other places a molecule would be able to hold on to only a single carbon atom. Under these conditions there will be some spaces from which evaporation of adsorbed molecules would occur very slowly and others from which it would take place much more rapidly. There would be, however, a fairly sharp limit to the number of molecules which could come into intimate contact with carbon atoms. This limit would correspond to the saturated state observable in adsorption even by porous bodies. But it is evident that Equations 14, 15 and 16 which apply to adsorption by plane surfaces, could not apply to adsorption by charcoal. The real reason for this failure is that we can no longer assume (as in the derivation of Equation 14) that the rate at which the adsorbed gas evaporates from the surface is proportional to the amount present on the surface.

Strong support for the above views on the structure of porous bodies and the nature of adsorption by them is furnished by experiments in which molybdenum filaments were vaporized in nitrogen at low pressures. These experiments will be described in a future publication.<sup>1</sup>

### General Conclusions Regarding Kinetics of Heterogeneous Reactions.

The theory developed in this paper and the experimental work on electron emission and chemical reactions at low pressures leads to the following conclusion: *In a heterogeneous chemical reaction, the activity of a surface depends in general upon the nature of, the arrangement of, and spacing of the atoms forming the surface layer.* The atoms forming the second layer below the surface are of importance only insofar as they determine the arrangement of the surface atoms.

In the second part of this paper, it will be shown that the surface tension in liquids depends upon these same factors, in other words, it de-

<sup>1</sup> A brief preliminary description of these results was given in *THIS JOURNAL*, 37, 1159 (1915).

pend<sup>o</sup>s primarily upon the *surface layer of atoms* and only secondarily upon the group molecules of which these atoms form parts.

According to this view, the velocity of reactions in general is not limited by the rate of diffusion through an adsorbed film, but by the rate at which the molecules strike (according to Equation 4) against that portion of the surface which is active. Of course, there are many chemical processes which are actually limited by physical factors, such as the rate of diffusion through layers of gas or moderately thick films covering the solids substances. The rusting of iron, the oxidation of aluminum, the solubility of very soluble salts, etc., are examples of this type. But there is no present justification for believing that such physical factors determine the velocity of the typical catalytic reactions.

This theory of heterogeneous reactions can be readily developed along quantitative lines. Some of the principles upon which this development is based have been outlined in a recent paper on the dissociation of hydrogen.<sup>1</sup> A brief, but more general treatment will, however, not be out of place here.

The velocity of a reaction usually depends on the fraction of the surface which is covered by adsorbed atoms or molecules. This in turn depends on the rate of condensation and on the rate of evaporation of the adsorbed substance. In the sections of this paper dealing with condensation and evaporation, we considered only the case where the vapor condensing and the surface on which condensation occurred, consisted of the same substance. In the case where different substances are involved, some additional factors must be taken into account.

*Condensation.*—The surface on which condensation occurs contains a definite number  $N_0$  of elementary spaces, per unit area. Let  $\theta$  be the fraction of these spaces which are unoccupied and  $\theta_1$  be the fraction occupied by adsorbed atoms or molecules.

If each molecule condensing requires only one elementary space, the rate of condensation will be equal to  $\alpha\theta\mu$ .<sup>2</sup> But it may happen that each molecule requires two such spaces before condensation can occur. The chance that one space will be vacant is  $\theta$ , but the chance that two given spaces will be simultaneously vacant is  $\theta^2$ . Therefore, the rate of condensation is equal to  $\alpha\theta^2\mu$ . In general, the rate of condensation will be  $\alpha\theta^n\mu$  where  $n$  is an integer.

*Evaporation.*—In evaporation it may occur that two atoms must lie in adjacent positions in order that they may leave the surface together as a molecule. In such cases the rate of evaporation will be  $\nu_1\theta_1^2$  instead of  $\nu_1\theta_1$ .

Chemical reactions may take place either between adjacent atoms

<sup>1</sup> THIS JOURNAL, 38, 1145 (1916).

<sup>2</sup> Compare with the derivation of Equation 14.

on the surface or may occur when gas molecules strike molecules or atoms on the surface. In the former case the velocity of the reaction, in general, will be proportional to  $\theta^n \theta_1^m \theta_2^p$  where  $\theta_1$  and  $\theta_2$  are the fractions of the surface covered by the reacting substances and  $n$ ,  $m$  and  $p$  are integers. The reason for the occurrence of the factor  $\theta^n$  in this expression is that the number of elementary spaces occupied by the products of the reaction may be greater than that occupied by the reacting substances. The reaction will thus only occur when vacant spaces are available.

We see that the reaction on surfaces will be governed by a "law of surface action" analogous to the "law of mass action." The velocity in both cases is proportional to a continued product of factors having integral exponents. A radical difference between the two laws exists in the presence of the factor  $\theta^n$  in the case of reactions on surfaces.<sup>1</sup>

Let us consider a few simple special cases of heterogeneous reactions.

To simplify the problem, we will assume that the velocity of the reaction is slow compared to the rate at which the gas condenses and evaporates from the surface. In other words, we will limit ourselves to a consideration of those cases where the velocity of the reaction is not fast enough to materially affect the equilibrium between the adsorbed film and the surrounding gas.

There are two types of cases to consider. First, those in which the adsorbed film covers only a very small fraction of the surface ( $\theta = 1$ ). Secondly, those in which the surface is nearly completely covered by the adsorbed film.

*First Case. Surface only covered to a small extent.*

Let us consider a single gas which undergoes a chemical change (for example a dissociation) in contact with a solid body. The rate of condensation on the surface will be  $\alpha_1 \mu_1$  and the rate of evaporation of the unchanged gas will be  $\nu_1 \theta_1^n$  where  $n$  represents the number of elementary spaces occupied by each molecule of the substance while on the surface. Then, since the adsorbed film is in equilibrium with the surrounding gas, we have<sup>2</sup>

$$\alpha_1 \mu_1 = \nu_1 \theta_1^n. \quad (17)$$

<sup>1</sup> Since  $\theta + \theta_1 + \theta_2 + \dots = 1$  this law bears a close relationship to Reichstein's "Constant Sum Hypothesis," which has been used to explain various kinds of passivity phenomena.

<sup>2</sup> This equation becomes identical with Equation 14 only when  $n = 1$  and  $\theta = 1$ . It is thus seen that the theory of adsorption which led to Equation 16 does not apply to the case where a molecule occupies more than one elementary space. Equation 17 shows that when  $n = 2$ , the amount of gas adsorbed is proportional to the square root of the pressure, even at very low pressures.

The equations that follow (19), (21), etc., may be derived in several different ways (see THIS JOURNAL, 38, 1149 (1916)) by making different kinds of assumptions. By experiment it will be possible to determine which set of assumptions correspond with the facts.



Now the product of the chemical reaction is formed from the adsorbed film by the combination of the substance from  $m$  adjacent spaces. In case of a dissociation  $m$  will be equal to unity. If  $\omega$  represents the velocity of the chemical change, we have

$$\omega = \nu_2 \theta_1^m. \quad (18)$$

Combining these two equations gives

$$\omega = \nu_2 \left( \frac{\alpha_1 \mu_1}{\nu_1} \right)^{m/n} \quad (19)$$

The velocity of the reaction thus varies with the  $m/n^{\text{th}}$  power of the pressure ( $\mu$ ) of the gas. In the case of the dissociation of hydrogen molecules by a heated wire, we have  $m = 1$  and  $n = 2$ , so that the velocity at which the gas is dissociated is proportional to the *square root* of the pressure of molecular hydrogen. The recombination of hydrogen atoms in contact with a heated wire, however, takes place in proportion to the *square* of the pressure of the atomic hydrogen. It has been shown previously that these conclusions are in accord with experiments.

Bodenstein and Ohlmer<sup>1</sup> mention that the velocity of the reaction between carbon monoxide and oxygen in presence of heated crystalline quartz is proportional to the pressure of the carbon monoxide and to the *square root* of the pressure of oxygen.

Now if we assume that each carbon monoxide molecule occupies one elementary space while each oxygen molecule occupies two (*i. e.*, is present on the surface in the form of atoms), we obtain

$$\begin{aligned} \alpha_1 \mu_1 &= \nu_1 \theta_1 \\ \alpha_2 \mu_2 &= \nu_2 \theta_2^2 \\ \omega &= \nu_3 \theta_1 \theta_2 \end{aligned} \quad (20)$$

where the subscript 1 refers to CO, 2 refers to O<sub>2</sub> and 3 refers to CO<sub>2</sub>.

These equations give

$$\omega = k \mu_1 \sqrt{\mu_2} \quad (21)$$

where  $k$  is a constant involving  $\alpha_1$ ,  $\alpha_2$ ,  $\nu_1$ , etc. Thus the relation found by Bodenstein and Ohlmer follows directly from the assumption that the oxygen adsorbed on the surface is present as separate atoms.

It has been found by Bodenstein and Kranendieck (p. 99 Nernst Festschrift) that the rate of decomposition of ammonia by heated quartz glass is proportional to the square root of the pressure. It will be shown in a subsequent paper that this fact is readily explainable by assumptions analogous to the above.

Freundlich and Bjercke<sup>2</sup> have recently found that the rate of oxidation of phenyl-thiourea by oxygen in contact with blood charcoal is proportional to the square root of the concentration of oxygen.

<sup>1</sup> *Z. physik. Chem.*, 53, 175 (1905).

<sup>2</sup> *Ibid.*, 91, 1 (1916).

It should be noted that the velocity of gas reactions is frequently proportional to the square root of the pressure, whereas according to the law of mass action, we should expect velocities proportional to some integral power of the pressure. The above theory of heterogeneous reactions offers a simple explanation of these fractional exponents. According to the Bodenstein-Fink theory of heterogeneous reactions, such square-root relations are to be explained by diffusion through films whose thickness varies in proportion to the square-root of the pressure. There is definite experimental evidence in the case of the dissociation of hydrogen (which gives a square root relation) that the adsorbed film covers only a very small fraction of the surface with a layer one atom deep. Hence the Bodenstein-Fink theory cannot possibly explain this case. It is very probable that such square root relations are never caused by diffusion through adsorbed films.

*Second Case. Surface nearly completely covered.*

Let us consider a reaction in which two gases are in contact with a solid body. One of the gases, which we shall designate by the subscript 1, is present in such quantity and evaporates so slowly from the surface that the surface remains nearly completely covered by an adsorbed film of this substance. A second gas, 2, undergoes a chemical change when its molecules come in contact with the uncovered surface. This reaction may be of several kinds. For instance, the gas molecules condensing in vacant spaces may dissociate, may react with the underlying solid, or may react with the adsorbed gas in adjacent spaces. The rate at which the first gas will condense is  $\alpha_1 \theta^n \mu_1$ , where  $n$  is the number of elementary spaces occupied by each molecule which condenses. The rate of evaporation will be constant  $\nu_1$ , since the surface is nearly covered. Therefore, for equilibrium

$$\alpha_1 \theta^n \mu_1 = \nu_1. \quad (22)$$

The rate at which the second gas will enter into reaction will usually be proportional to  $\theta \mu$ . It is quite possible, however, in some cases that  $\theta$  may have any integral or even fractional exponent. We thus obtain for the rate of reaction

$$\omega = \nu_2 \theta \mu_2. \quad (23)$$

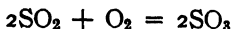
Combining these equations we find

$$\omega = \nu_2 \mu_2 \left( \frac{\nu_1}{\alpha_1 \mu_1} \right)^{1/n}. \quad (24)$$

The velocity of the reaction is thus proportional to the pressure of gas 2, and *inversely proportional to the  $n^{\text{th}}$  root of the pressure of gas 1.*

Now this is a relation which has been found to hold for a very great number of heterogeneous reactions in which the velocity is influenced by catalytic poisons. A few of these will be briefly mentioned.

Fink<sup>1</sup> found in the case of the reaction (in contact with platinum)



that the velocity is proportional to the pressure of  $\text{SO}_2$  and inversely proportional to the square root of the pressure of  $\text{SO}_3$ . This relation follows directly from Equation 24 if we place  $n = 2$ . We may thus conclude that the platinum surface was practically completely covered by a layer of adsorbed  $\text{SO}_3$  in which each molecule of  $\text{SO}_3$  required two elementary spaces for its condensation. Fink actually measured the amount of adsorbed  $\text{SO}_3$  and found it to be of the order of magnitude of a single layer of molecules. According to the Fink-Bodenstein theory, the amount of adsorbed  $\text{SO}_3$  in these experiments should have been proportional to the square root of the  $\text{SO}_3$  pressure, whereas according to the above theory the amount adsorbed should have been practically independent of the pressure (saturation). It is, however, obvious that a film one molecule thick (as found by Fink) cannot have a *thickness* which varies in proportion to the square root of the pressures over a wide range.

Bodenstein and Ohlmer found that the reaction between oxygen and carbon monoxide in contact with quartz glass takes place at a rate proportional to the pressure of oxygen and inversely proportional to the pressure of carbon monoxide. Evidently here  $n = 1$  so that each molecule of carbon monoxide occupies only one elementary space.

The writer has found<sup>2</sup> that the same relation holds when these gases react with each other at very low pressures in contact with platinum. It was also found<sup>3</sup> that in the catalysis of oxygen-hydrogen mixtures by a platinum wire, the velocity is proportional to the pressure of oxygen and inversely proportional to that of the hydrogen.

An interesting application of this theory arises in connection with enzyme action. The velocity of many of these reactions varies in accordance with Schutz's rule.<sup>4</sup> Consider a reaction in which a substance A is converted into B by the action of an enzyme. Let  $x$  be the amount of B formed in the time  $t$ , assuming that the substance B is absent when  $t = 0$ . Let  $E$  be the amount of enzyme present. Then according to Schutz's rule

$$x = k\sqrt{Et}. \quad (25)$$

Thus the amount of B formed is independent of the concentration of A, but is proportional to  $\sqrt{Et}$ .

By squaring and differentiating (25) we obtain, if  $E$  remains constant

<sup>1</sup> Dissertation, Leipzig, 1907; see also Bodenstein and Fink, *Z. physik. Chem.*, **60**, 1 (1907).

<sup>2</sup> THIS JOURNAL, **37**, 1162 (1915).

<sup>3</sup> More recent experiments show that this is not the usual manner in which hydrogen and oxygen react in contact with platinum even at low pressures. The factors which cause the above type of reaction have not yet been determined with certainty.

<sup>4</sup> See Euler, *Allgemeine Chemie der Enzyme*, pp. 125, 106 and 113.

$$\frac{dx}{dt} = \frac{1}{2} k^2 \frac{E}{x}. \quad (26)$$

Thus another way of stating Schutz's rule is to say that the velocity of the reaction is proportional to the amount of enzyme, is inversely proportional to the amount of B formed, and is independent of the amount of A.

It is generally recognized that enzymes are colloids on the surfaces of which reactions occur. We may thus interpret Schutz's rule as an indication that the product B of the reaction is adsorbed on the surface of the colloidal particles forming a layer one molecule deep nearly completely covering the surface. By comparing Equations 26 and 24 we see that  $n = 1$  from which we conclude that each adsorbed molecule occupies only one elementary space. The reaction thus takes place only on that fraction of the surface which is not covered by molecules of B.

By Equation 24 we should expect the velocity of the reaction to be proportional to the concentration of A, but according to Schutz's rule the velocity is independent of this concentration. This seems somewhat difficult to explain. It is, perhaps, possible that molecules of A are adsorbed over practically all the surface not occupied by B, and that molecules of B are able to *displace* molecules of A thus adsorbed. Let  $\theta_a$  and  $\theta_b$  be the fractions of the surface covered by A and B, respectively. Then according to the above hypothesis, we would have

$$\alpha_b \theta_a \mu_b = \nu_b \theta_b. \quad (27)$$

$$\omega = \nu_a \theta_a. \quad (28)$$

Since  $\theta_b$  is nearly equal to unity, we thus have

$$\omega = \left( \frac{\nu_a \nu_b}{\alpha_b} \right) \frac{1}{\mu_b}, \quad (29)$$

which is of exactly the same form as (26) and is thus equivalent to Schutz's rule.

#### SUMMARY.

1. The work of the Braggs on crystal structure is reviewed from the viewpoint of the chemist and the relation of this work to theories of chemical constitution such as those of Werner, Stark, J. J. Thomson, and Lewis, is discussed in detail.

2. It is concluded that the substances whose structures have thus far been studied by the X-ray spectrograph are not representative of compounds in general. Only polar compounds have been studied.

3. Solid polar compounds are, in general, built up of atoms bound together by secondary or residual valence. The whole crystal must be regarded as a single molecule.

4. Solid nonpolar compounds consist in general of "Group Molecules" in which the atoms are usually held together by primary valence. These

group molecules in turn are bound together by secondary valence to form a large "Crystal Molecule," which includes the whole solid mass.

5. There is no present justification for dividing interatomic (or intermolecular) forces into *physical* and *chemical* forces. It is much more profitable to consider all such forces as strictly chemical in nature. Evaporation, condensation, solution, crystallization, adsorption, surface tension, etc., should all be regarded as typical chemical phenomena. The object of this paper is largely to show that *chemical knowledge already available* is directly applicable to the study of these phenomena.

6. From a consideration of such properties as specific heat, compressibility, coefficient of expansion, etc., it is concluded that collisions do not take place between the atoms of solids, but that these move about equilibrium positions under the influence of both attractive and repulsive forces.

7. The "time of relaxation" of the atoms of solids is calculated approximately from the heat conductivity and is found to be of the order of  $10^{-14}$  to  $10^{-7}$  seconds. An independent method by which the "time of relaxation" can be calculated from the rate of evaporation of a substance in vacuum, gives substantially similar results. Thus the time necessary for an atom of a solid to reach thermal equilibrium with its neighbors is very small compared to the time necessary to make a single oscillation about an equilibrium position. The "oscillations" are thus extremely strongly damped.

8. Since solid substances in general are held together by secondary rather than primary valence, there are few limitations to the number of compounds that can exist in the solid state. Most of these compounds do not show a composition which could be predicted from the ordinary rules of valence. Metallic compounds, minerals, solid solutions and glasses are discussed from this point of view.

9. By considerations based largely on the compressibility, it is concluded that the attractive forces between atoms usually reach a maximum intensity when the distance between adjacent atoms in solids is increased by about  $0.6 \times 10^{-8}$  cm. (10-30% of the normal distance between atoms).

10. Since energy must be expended in breaking apart a solid, the surfaces of solids must contain more potential energy than do the corresponding number of atoms in the interior. Since this potential energy is probably electromagnetic energy in the field between atoms, the interatomic forces are more intense on the surface than in the interior. This intense surface field of force (unsaturated chemical affinity) is one of the causes of the phenomena of condensation and adsorption.

11. Because of the small time of relaxation and because an atom approaching the surface is attracted by many, but later is repelled by few

atoms, it follows that the surfaces of solids are almost wholly inelastic in regard to collisions of molecules impinging on the surface. There is also a great deal of experimental evidence of this inelasticity. As a result, nearly every molecule or atom striking a solid surface condenses no matter what the temperature may be. While condensed it is held to the surface by forces quite similar to those holding solids together (either primary or secondary valence). At high temperatures evaporation may take place almost immediately after condensation, but at lower temperatures, the condensed atom or molecule may remain indefinitely.

12. The phenomena of condensation and evaporation (sublimation) of solids is discussed at some length. In general, the rate of evaporation ( $m$ ) of a substance in a high vacuum is related to the pressure ( $p$ ) of the saturated vapor by the equation

$$m = \sqrt{\frac{M}{2\pi RT}} p.$$

Red phosphorus and some other substances probably form exceptions to this rule.

13. The mechanism of the dissociation of a solid, such as  $\text{CaCO}_3$  is discussed. It is shown that when, according to the phase rule, separate phases of constant composition are present, the reaction must take place exclusively at the boundaries of these phases. This kinetic interpretation of the phase rule indicates clearly the distinction between reactions in which solid solutions are formed and those in which separate phases appear. This theory offers a ready explanation for the fact that hydrated crystals frequently fail to effloresce unless scratched and for the fact that thoroughly dehydrated substances often absorb moisture with great difficulty.

14. Adsorption is a direct consequence of the time lag between the condensation and the subsequent evaporation of molecules. The adsorbed substance may be held to the surface either by secondary or primary valence. In either case it is profitable to regard the phenomena as chemical in nature. A large number of experimental results are given which prove conclusively that adsorption is very frequently the result of the strongest kind of chemical union (primary valence) between the atoms of the adsorbed substance and the atoms of the solid.

15. It is shown that the action of a typical catalytic poison depends on the formation of a very stable film one atom deep over the surface of the catalyzer. The chemical activity of any solid surface depends upon the nature of, the arrangement of, and the spacing of the atoms forming the surface layer. There is a very close relation between the chemical activity of a surface and the electron emission from it (either thermionic or photoelectric emission).

16. A brief quantitative development of this theory of heterogeneous reactions is given. A "law of surface action" analogous to but different

from, the "law of mass action" is proposed. This theory is in accord with and affords an explanation of Reichinstein's "Constant Sum Hypothesis." An outline is given of the application of this theory to heterogeneous gas reactions and to enzyme action.

The second part of this paper will deal with the Structure of Liquids with particular reference to surface tension phenomena. It will be shown that the surface tension of organic liquids is a characteristic *chemical* phenomena. It depends particularly upon the *shapes* of the group molecules and upon the relative intensities of the chemical activity of *different portions* of the molecules. A method will be described (together with experimental data) by which the *cross sections*, *lengths* and other dimensions of group molecules of liquids may be determined.

SCHENECTADY, N. Y.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, PRINCETON UNIVERSITY.]

## THE THERMODYNAMIC PROPERTIES OF SILVER AND LEAD IODIDES.

By HUGH STOTT TAYLOR.

Received July 10, 1916.

The thermodynamic properties of silver and lead iodides have been the subject of considerable recent experimental investigation. The object of the work has been to obtain accurate data on the free energies and heats of formation with a view to testing the newer thermodynamic conceptions relative to these two magnitudes.

The relation between free energy and heat of formation is representable, according to the two laws of thermodynamics, by the fundamental equation,

$$A - U = T dA/dT.$$

With the aid of this equation, given the maximum work or free energy,  $A$ , at any temperature,  $T$ , together with its temperature coefficient  $dA/dT$ , it is possible to evaluate the heat effect of the reaction  $U$ . The values obtained by such a procedure should show concordance with the direct calorimetric observations. Alternatively, if it be desired to proceed from the thermal data to an evaluation of the free energy, classical thermodynamics, without the aid of new assumptions, is inadequate. This will readily be grasped if the form of the above equation be somewhat modified. Since

$$A - U = T dA/dT,$$

it follows that

$$A dT - T dA = U dT,$$

Dividing each side by  $T^2$  there results,

$$\frac{A \, dT - T \, dA}{T^2} = \frac{U \, dT}{T^2},$$

whence

$$A = -T \int \frac{U \, dT}{T^2} + IT$$

where  $I$  is the constant of integration.

Obviously, in order to evaluate  $A$  from the thermal data it is necessary to know  $U$  as a temperature function and also the value of the integration constant  $I$ . As regards the variation of  $U$  with temperature it is well known that this magnitude varies with the specific heats of the reacting substances (Kirchhoff's Law) according to the equation

$$dU/dT = \Sigma nC$$

the summation sign indicating an algebraic summation (reactants positive, resultants negative) of the molecular heats of the substances participating, multiplied by their respective molecular coefficients,  $n$ . The necessity of evaluating this equation has led to the determination of specific heats of many substances down to very low temperatures with a resultant considerable development in the theory of specific heats, some of the newer features of which will later be developed. Concerning the constant of integration,  $I$ , classical thermodynamics teaches nothing. New assumptions are necessary, the consequences of which must be submitted to experimental verification before they are finally accepted.

The fundamental assumption made by Nernst in the Nernst heat theorem is

$$\lim (dU/dT) = \lim (dA/dT) \text{ for } T = 0$$

for all reactions which take place in condensed systems, *i. e.*, in systems which persist continuously, without change of state of aggregation, down to the absolute zero of temperature. Obviously, therefore, this assumption applies to reactions between pure solids and liquids which supercool but not to those between gases and solutions. The deductions which may be made from this assumption are independent of the manner in which  $A$  and  $U$  are expressed as functions of temperature provided the functions be continuous. Thus, the fundamental thermodynamic equation may be generalized to give

$$\varphi(T) = f(T) + T\varphi'(T),$$

in which  $A = \varphi(T)$ ,  $U = f(T)$ , and  $dA/dT = \varphi'(T)$ .

This yields on differentiation,

$$\varphi'(T) = f'(T) + T\varphi''(T) + \varphi'(T)$$

whence

$$\varphi''(T) = -1/T \cdot f''(T).$$

If this equation be integrated, there follows

$$\varphi'(T) = - \int 1/T \, f''(T) dT + I.$$



For the small temperature  $dT$  above the absolute zero, this equation yields

$$\varphi'(dT) = -f'(dT) + I,$$

which is only reconcilable with the assumption of Nernst, *i. e.*,

$$\lim f'(T) = \lim \varphi'(T) \text{ for } T = 0$$

if,

$$(a) \lim \varphi'(T) = \lim f'(T) = 0$$

and

$$(b) I = 0.$$

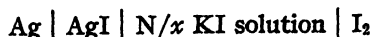
Accordingly, if the Nernst hypothesis be accepted, it follows that the integration constant is zero and the evaluation of free energy from thermal data becomes at once possible when  $U$  is known as a temperature function since the  $IT$  term of the original equation becomes zero and consequently,

$$A = -T \int_0^U \frac{dT}{T^2}$$

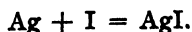
Nernst was led to his assumption reasoning from the approximate equality of  $A$  and  $U$  at moderate temperatures with reactions between solids and pure liquids in agreement with the Berthelot principle. Its final acceptance or rejection will depend however on experimental verification, to which end accurate determinations of heats of reaction, free energies and specific heats will all be requisite.

For such purposes of experimental measurement the halides of several of the metals have been eminently suitable owing to the relative simplicity of structure and of the reactions which result in their formation and interaction. Also, they have proved suitable for direct determination of the free energy magnitudes and of the calorimetric data. In the case of one of these salts, silver iodide, an examination of the literature reveals that the conclusions reached by different workers as a result of careful experimental investigation are not only not concordant but are actually diametrically opposed as to the value which must be assigned to the integration constant.

Ulrich Fischer in a research on the affinity between iodine and silver<sup>1</sup>—elsewhere characterized by Nernst as “*der sehr eingehend und genau untersuchte Fall der Bildung des Jodsilbers*”—determined electrometrically and with the aid of the fundamental thermodynamic equation by measurements of the electromotive force and temperature coefficient of cells of the type



the heat of the reaction



This was supplemented by a calorimetric determination of the same

<sup>1</sup> *Z. anorg. Chem.*, 78, 41 (1912).

quantity. Concordant values by both methods yielded as a mean for  $T = 288^\circ \text{K.}$  a value for  $U$  of 15,000 calories with a maximum deviation from the mean of 180 calories. Calculating from the electromotive forces of the cells with the aid of the Nernst heat theorem (assuming  $I = 0$ ) a value of 15,079 calories was obtained, forming strong evidence in support of the truth of the theorem.

More recently, a publication by Jones and Hartman<sup>1</sup> described similar measurements with cells of the same type, though different in construction, for which a considerably higher degree of constancy and reproducibility is claimed than was obtained by Fischer. From measurements of the electromotive force at two temperatures with the aid of the most reliable specific heat data it was concluded that the integration constant was not zero but had a value equal to 2.33 calories per degree, so that in the free energy equation not only was  $IT$  not equal to zero but on the contrary at  $273^\circ \text{K.}$  possessed a value  $273 \times 2.33 = 636$  calories, greater in magnitude than the sum of all the terms involving the specific heats of the substances concerned.

It is evident therefore that between these two investigations there exists a considerable discrepancy which is more manifest in view of the following considerations. Calculation with the aid of the Gibbs-Helmholtz equation using the values for  $A$  and  $dA/dT$  obtained by Jones and Hartmann yields as a mean value for  $U$  the heat of reaction, 14,565 calories, a deviation from the mean obtained by Fischer of 435 calories. Independently, and apparently overlooked by Jones and Hartmann, the calorimetric determination of the heat of formation of silver iodide was carried out by Braune and Koref<sup>2</sup> and found to be 15,100 calories, somewhat higher than that determined by Fischer using the same method, and deviating still further from the value of Jones and Hartmann. With the aid of new determinations of the specific heat of silver iodide, Braune and Koref recalculated the value of  $U$  according to the Nernst heat theorem and obtained a value, 15,188 calories.

The divergencies between the three sets of data are readily grasped from the following table:

$U$ from $dA/dT$ and $A$ .	$U$ thermo- chemically.	$U$ from Nernst heat theorem.	Author.
15169	14820	15079	Fischer
...	15100	15135	Braune & Koref
14565	...	14500	Jones & Hartmann

The values of Jones and Hartmann have been calculated by the author from their electromotive force data and according to the theorem from their value for  $U_0$ , since they did not attempt determination of  $U$  but

<sup>1</sup> *THIS JOURNAL*, 37, 752 (1915).

<sup>2</sup> *Z. anorg. Chem.*, 87, 175 (1914).

concentrated attention on the method for determining  $I$  from measurements of the temperature coefficients of the cells.

It will be obvious that any experimental evidence which can help to a decision on the merits of the several sets of determinations will be of extreme importance, since the conclusions from these investigations involve important evidence on the general theorem that  $I = 0$ .

From the researches of Jones and Hartmann it would seem that the integration constant is not equal to zero, while the work of Fischer and of Braune and Koref suggests the opposite conclusion. This latter verdict is supported by work of Braune and Koref on the corresponding reaction with lead and iodine. In a manner similar to that employed by Fischer they investigated calorimetrically the heat of formation of lead iodide and also the electrometric relationships of cells of the type



using, to attain reproducible electrodes, 0.72 per cent. lead amalgam instead of lead. The results obtained were reduced to those of metallic lead electrodes by use of the accurate data of Brönsted<sup>1</sup> on the e. m. f. of lead—lead amalgam cells. Concordant results were obtained by the several methods and they agreed with the value calculated from the Nernst theorem as the following summary shows:

REACTION:  $\text{Pb} + \text{I}_2 = \text{PbI}_2$  ( $T = 293^\circ \text{K.}$ ).

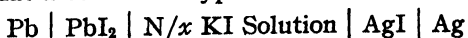
From  $TdA/dT = A - U$ .....  $U = 41960$  calories.

Thermochemically.....  $U = 41850$  calories.

According to the theorem.....  $U = 42034$  calories.

In the present research an attempt has been made to throw light on the point at issue by investigation of a cell which consists essentially of a combination of the two cells previously discussed. It was apparent that if such a cell could be constructed and yielded constant and reproducible results information would be obtained allowing of a test of the two earlier combinations.

It is evident that a cell of the type



possesses certain advantages over cells of the type

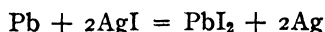


since by elimination of the iodine electrode there is eliminated from the system a liquid potential effect at the junction of the two halves of the cell and also an osmotic work effect caused by the different concentrations of iodide ions on the two sides. The corrections for these two effects are considerable and, at the same time, are uncertain as compared with the accuracy with which the cells may be reproduced. Thus, in the cell of Jones and Hartmann with 0.05  $N$  KI at  $25^\circ \text{C.}$  the liquid poten-

<sup>1</sup> *Z. physik. Chem.*, 56, 668 (1906).

tial correction amounted to +0.0032 volt while the osmotic work correction amounted to -0.0177 volt, a considerable percentage of the total e. m. f. measured, *viz.*, 0.6992 volt. On the contrary, with insoluble salts like silver and lead iodides a homogeneous electrolyte was readily obtainable and the various corrections disappear.

From a determination of the electromotive force of the combination and its temperature coefficient, a value for the heat of the reaction



may be deduced. The results obtained may then be compared with the electrometric and calorimetric data previously detailed and may also be employed in calculations according to the Nernst theorem. In the following the results of such an investigation are presented.

### Experimental.

**Preparation of the Silver-Silver Iodide Electrodes.**—Constant and reproducible silver electrodes were readily obtained, after a little experience, by following closely the detailed directions supplied by Jones and Hartmann, so that the method of preparation does not call for further detailment here. The reproducibility obtained was excellent as the table below shows. The several electrodes (5-9) were separately and successively made from June 2nd to 4th. After preparation, they were kept in a solution of potassium iodide saturated with silver iodide and of the same normality as that in which it was designed to use them.

Electrode 5 against.....	6	7	8	9
June 7th. Difference.....	-0.00002	+0.00006	+0.00002	+0.00003
The maximum difference of any pair is 0.00008 volt.				
The average difference from the mean is 0.00002 volt.				

**The Lead Amalgam Electrodes.**—Lead amalgam was prepared, of strength exactly 0.72% lead by weight, from three times distilled mercury and the very purest lead procurable. The lead employed was bright and lustrous, the coating of oxide being removed from the sample from which the lead employed was cut. The amalgam showed a marked tendency to oxidize. If made in contact with the air it was soon covered with oxidation products. Accordingly, the weighed quantity of mercury was covered with a solution of potassium iodide of the same strength as was later to be used with the amalgam in the cells. From this solution the oxygen was removed by bubbling through pure hydrogen, after which the lead was added in small pieces and in the calculated amount. Hydrogen was bubbled through until the amalgam was homogeneous. By this method of preparation clean bright amalgam was obtained. Its constancy and reproducibility is manifest from the constancy of the complete element described below.

**The Cell.**—Since the solution could be homogeneous and it was necessary only to limit the diffusion between the two electrodes, the H type

of cell was chosen. Into one limb the amalgam was introduced, contact with the outside being established by means of a platinum wire sealed through the base of the limb. Over the amalgam was placed, about 1 cm. deep, a layer of a paste composed of lead iodide and the solution of potassium iodide of the normality chosen. Each limb was then filled to the cross-piece with a solution of potassium iodide saturated, the one with silver iodide, the other with lead iodide, the latter naturally over the lead amalgam. Contact between the two limbs was then made by filling the H-piece carefully with the pure potassium iodide solution. Into the limb containing the silver iodide in potassium iodide the silver-silver iodide electrode was introduced. The electrode was held in position by means of a cork which served also to close the limb. The other limb was closed by means of an ordinary cork stopper. After setting up, the cells were immediately placed in an oil-bath thermostat regulated carefully to  $25^{\circ} \pm 0.01^{\circ}$ .

The potentials of the cells immediately after setting up were low and varied among themselves, but rose steadily to constant and concordant values. The cells apparently maintain their constancy for a considerable period of time and with varying treatment. The tables communicated below show that after a series of constant measurements extending over several days had been obtained at  $25^{\circ}$  C. the cells gave concordant values for a further period of time at  $0^{\circ}$ , returning to their original values when replaced in the  $25^{\circ}$  thermostat.

Two strengths of potassium iodide solution were used, 0.1 and 0.05 *N*. As regards constancy, there is little to choose between the two dilutions. Tables I and II record typical measurements at  $0^{\circ}$  and  $25^{\circ}$  with the two sets of cells.

TABLE I.  
0.05 *N* Potassium Iodide Solution.

Cell No. ....	1	2	3	4	5	
Silver Electrode No. ....	5	6	7	8	9	
Date of construction.	Temp.	June 7th.	June 7th.	June 7th.	June 7th.	
June 8th, A.M. ....	25°	0.19860	0.19995	0.19915	0.19833	0.19817
8th, P.M. ....	25	0.20051	0.20050	0.20044	0.20031	0.20037
9th, A.M. ....	25	0.20067	0.20072	0.20056	0.20054	0.20050
9th, P.M. ....	25	0.20070	0.20072	0.20065	0.20057	0.20060
10th, P.M. ....	25	0.20076	0.20072	0.20056	0.20064	0.20065
11th, P.M. ....	25	0.20075	0.20075	0.20062	0.20065	0.20065
12th, A.M. ....	25	0.20065	0.20065	0.20056	0.20065	0.20055
13th, A.M. ....	25	0.20058	0.20058	0.20067	0.02071	0.20045
Placed in ice June 13th, A.M.						
June 13th, P.M. ....	0°	0.2093	0.2096	0.2094	0.2099	0.2096
14th, A.M. ....	0	0.20930	0.20964	0.20965	0.20993	0.20968
14th, P.M. ....	0	0.20926	0.20965	0.20980	0.20985	0.20977
15th, P.M. ....	0	0.20930	0.20982	0.20955	0.20985	0.20978
Replaced in bath at 25°.						
June 17th, P.M. ....		0.20046	0.20035	0.20049	0.20078	0.20066

TABLE II.  
0.10 N Potassium Iodide Solution.

Cell No.....		9	10	12	13	14
Silver Electrode No.....		13	14	10	11	12
Date of construction.	Temp.	June 11th.	June 11th.	June 15th.	June 15th.	June 15th.
June 12th, A.M.....	25°	0.19982	0.19980	...	...	...
13th, A.M.....	25	0.19995	0.19973	...	...	...
14th, A.M.....	25	0.20010	0.19950	...	...	...
15th, A.M.....	25	0.20014	0.19950	...	...	...
16th, A.M.....	25	0.20013	0.19920	0.19823	0.19865	0.19814
17th, A.M.....	25	0.20006	0.19293	0.19944	0.19974	0.19964
18th, A.M.....	25	0.20003	0.09526	0.19946	0.19975	0.19976
19th, A.M.....	25	0.20008	0.11500	0.19959	0.19988	0.19978
20th, P.M.....	25	0.20003	Discontinued.	0.19959	0.19988	0.19980
Placed in ice June 21st, A.M.						
June 21st, P.M.....	0	0.20932	...	0.20906	0.20904	0.20890
22nd, A.M.....	0	0.20925	...	0.20905	0.20894	0.20890
22nd, P.M.....	0	0.20931	...	0.20908	0.20908	0.20903
23rd, A.M.....	0	0.20922	...	0.20896	0.20904	0.20909
24th, A.M.....	0	0.20909	...	0.20890	0.20900	0.20903
25th, P.M.....	25	0.19998	...	0.19965	0.20003	0.19969

A certain percentage of the cells set up showed initially a normal potential, but, in the course of a few days fell away in electromotive force and gave irregular and fluctuating values. In several cases this was identified with the passage of suspended silver iodide through the H-piece and deposition on the lead iodide. Presumably when this penetrated thus far the irregularities observed were obtained. A typical example of this behavior is recorded in Table II, Cell 10.

The potential measurements were made with the aid of a Wolff direct-reading potentiometer and a Leeds and Northrup high sensitivity galvanometer. For the potentiometer settings, use was made of the exceptional facilities of this laboratory in the matter of standard cells, so that the electromotive forces determined could readily be checked to the hundredth of a millivolt.

In Table III are recorded the accepted means for the different cells at the two temperatures and the accepted means for the two combinations.

TABLE III.  
0.05 N KI solution.                      0.10 N KI solution.

Cell No.	Accepted value, 0°.	Accepted value, 25°.	Cell No.	Accepted value, 0°.	Accepted value, 25°.
1.....	0.20930	0.20069	9.....	0.20920	0.20006
2.....	0.20965	0.20069	12.....	0.20900	0.19950
3.....	0.20965	0.20060	13.....	0.20900	0.19979
4.....	0.20990	0.20060	14.....	0.20905	0.19972
5.....	0.20971	0.20057	.....	...	...
Mean value..	0.20965	0.20065	.....	0.20905	0.19977

Cells were set up in which water was used as the liquid medium but neither constancy nor reproducibility was attainable. This is doubtless due to secondary reactions—probably at the amalgam electrode—as it was found that in preparing the amalgam in the manner previously described, if distilled water were used as the protecting liquid, lead hydroxide readily formed and was noted by the resulting cloudiness of the aqueous layer. The small solubility of the two iodides may also have contributed to the observed irregularities.

### Evaluation of the Results.

To convert the values obtained with the amalgam cells to those obtaining in the case of metallic lead as electrode, use was made of the formula of Brönsted for lead—lead amalgam cells. Brönsted showed that such cells gave constant and reproducible values over a wide temperature range, representable by a linear interpolation formula

$$E = 0.0051 + 0.000233t,$$

where  $t$  is the temperature in degrees centigrade. Hence it follows, that to the observed means in the present series must be added (a) at  $0^\circ$  0.0051 volt, and (b) at  $25^\circ$  0.01092 volt. This yields for the electromotive forces of the combinations  $\text{Pb} \mid \text{PbI}_2 \mid N/x \text{ KI} \mid \text{AgI} \mid \text{Ag}$ .

$$(a) \quad x = 0.05. \quad \begin{array}{l} \text{At } 25^\circ \text{ 0.21157 volt.} \\ \text{At } 0^\circ \text{ 0.21475 volt.} \end{array}$$

$$(b) \quad x = 0.10. \quad \begin{array}{l} \text{At } 25^\circ \text{ 0.21069 volt.} \\ \text{At } 0^\circ \text{ 0.21415 volt.} \end{array}$$

The temperature coefficients of the two combinations are, respectively,

$$(a) \quad \frac{0.21157 - 0.21475}{25} = -0.000127 \text{ volt per degree.}$$

$$(b) \quad \frac{0.21069 - 0.21415}{25} = -0.000138 \text{ volt per degree.}$$

These two sets of data, when employed in the Gibbs-Helmholz equation, give values for  $U$

$$(a) \quad 11500 \text{ calories.} \quad (b) \quad 11610 \text{ calories.}$$

The mean value for  $U$  from the two sets of determinations is, therefore,

$$U = 11550 \pm 50 \text{ calories,}$$

which represents the heat of the reaction



as determined by means of the cell combination employed.

A comparison of this value with the data obtained from the previously tabulated results of Fischer, Braune and Koref, and Jones and Hartmann is most interesting.

Calorimetrically, from the data of Braune and Koref one obtains

$$U = 41850 - 2(15100) = 11650 \text{ calories}$$

in good agreement with the value found above.

Combining the electrometric data of Fischer and Braune and Koref, there results

$$U = 41960 - 2(15170) = 11620 \text{ calories,}$$

also in good agreement with the observed value.

Combining the electrometric data of Braune and Koref with those of Jones and Hartmann for silver iodide there results

$$U = 41960 - 2(14565) = 12830 \text{ calories,}$$

or a discrepancy of more than 1000 calories.

This conclusion is somewhat anomalous, judged from the standpoint of the experimental work, since the determinations of Jones and Hartmann are, apparently, considerably more concordant and reproducible than are those of Fischer, while those of the present work are comparable in every way with those of Jones and Hartmann in this regard.

It should be observed that both Fischer, and Braune and Koref omitted to allow for the liquid potential effect and that therefore their results are in error to the extent of about 3 millivolts or about 0.4 % in the case of the silver cell and 0.3 % in the case of the lead cell. Further, according to Jones and Hartmann, the correction employed by the earlier workers for the osmotic work due to the presence of triiodide causes an error in the value for the electromotive force of the cell and also in the value for the temperature coefficient. These facts vitiate any combination of the measurements of Jones and Hartmann with those of Braune and Koref.

Recalculating the results of Fischer in accordance with the method of Jones, it can readily be shown that  $U$  in the Gibbs-Helmholz equation would be 15010 calories or 200 calories less than the value deduced by Fischer. Since Braune and Koref adopted the same procedure as Fischer with regard to the two effects it is evident that the error thus caused in their value for  $U$  will be of the same magnitude. This brings down the discrepancy between the experimental values obtained in the present work and those derived from the values of Jones and Hartmann and of Braune and Koref to somewhat more than 600 calories, a still quite definite discrepancy.

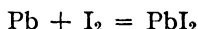
An error of this number of calories in the electrometric determination of  $U$  for lead iodide by Braune and Koref would bring agreement between the present work and that of Jones and Hartmann. It would then be necessary to locate the divergencies between the calorimetric data and the electrometric data in the cases of the two iodine cells. The presence of polyiodides in the iodine cells and their absence in the calorimetric method (since the values were obtained from the heats of solution



of iodine plus silver and of silver iodide in a solution of potassium cyanide) might contribute to such a discrepancy. Also, the possibility of the calorimetric data being affected by side reactions between iodine and potassium cyanide is not wholly excluded.

The data which have been obtained have also been utilized in an effort to determine the magnitude of the integration constant of the thermodynamic equation. The calculation has been carried out by each of two methods, that employed by Nernst and that of Jones and Hartmann. The results are not without interest.

In the first place, the data compiled by Braune and Koref have been combined and applied to the present reaction. Thus, for the reaction



it was shown that the following relations hold, assuming  $I = 0$ :

$$(1) \quad A_0 = A_{293} + 654 \text{ calories.}$$

$$(2) \quad U_{293} = U_0 + 160 \text{ calories.}$$

Correspondingly for the formation of silver iodide it was calculated

$$(1) \quad A_0 = A_{293} - 487 \text{ calories.}$$

$$(2) \quad U_{293} = U_0 - 40 \text{ calories.}$$

Combining these two sets of data it is apparent that for the new reaction

$$(1) \quad A_0 = A_{293} + 654 - 2(-487) \text{ calories} \\ A_{293} + 1628 \text{ calories.}$$

and

$$(2) \quad U_{293} = U_0 + 160 - 2(-40) \\ U_0 + 240 \text{ calories.}$$

By interpolation from the experimental results it is found that

$$(a) \quad \text{For } 0.05 \text{ } N \text{ KI} \quad A_{293} = 9870 \text{ calories.}$$

$$(b) \quad \text{For } 0.10 \text{ } N \text{ KI} \quad A_{293} = 9840 \text{ calories.}$$

Or, in the mean

$$A_{293} = 9855 \text{ calories.}$$

Hence,

$$A_0 = 9855 + 1628 = 11483 \text{ calories.}$$

and therefore

$$U_{293} = 11483 + 240 = 11723 \text{ calories.}$$

This value differs from the experimentally determined value by 173 calories, 1.5% of the total value, and from the calorimetrically determined value by 73 calories (0.6%), which must be considered in view of the uncertainty of specific heat data a satisfactory agreement.

In the second place use has been made of the procedure adopted by Jones and Hartmann for evaluation of  $I$  from measurements of the electromotive force at two temperatures, and insertion of the experimentally determined values in the corresponding equations for  $A$ . In this manner two equations are obtained of the form

$$A = U_0 + IT + \text{Terms involving the specific heats,}$$

from which  $U_0$  may be eliminated and the equations solved for  $I$ . The

procedure is in reality the accurate determination of  $dA/dT$ , the equation for which does not involve any term containing  $U_0$ , to which, it is claimed, an error of many hundred calories may be attached.

For the evaluation of the terms in the equation relative to the heat capacities of the reacting substances the formula of Debye for specific heats was used, since as was shown by Nernst and Lindemann<sup>1</sup> this formula gives the best representation of the experimental values at extremely low temperatures. The mode of employment of the Debye equation has been demonstrated by Nernst.<sup>2</sup> The formula for the specific heat as used by him is as follows:

$$C_v = 3R \left( \frac{4\pi^4}{5} \left( \frac{T}{\beta\nu} \right)^3 - \frac{3\beta\nu/T}{e^{\beta\nu/T} - 1} - \frac{1}{12} \frac{\beta\nu}{T} \sum_{n=1}^{\infty} e^{-n\beta\nu/T} \left( \frac{1}{n\beta\nu/T} + \frac{3}{n^2(\beta\nu/T)^2} + \frac{6}{n^3(\beta\nu/T)^3} + \dots \right) \right)$$

which is derived from the Debye equation for  $U$

$$U = \frac{9}{12} R \left( \frac{C_v}{C_\infty} + \frac{3x}{e^x - 1} \right) T$$

where  $x = \beta\nu/T$  and  $C_\infty = 3R$ .

Developed as a series, this gives

$$U = 0.75 \beta\nu R \left( \frac{77.94}{x^4} - \frac{1}{12} \sum_{n=1}^{\infty} e^{-nx} \left( \frac{1}{nx} + \frac{3}{n^2x^2} + \frac{6}{n^3x^3} + \frac{6}{n^4x^4} \right) \right).$$

The integration of this formula according to the thermodynamic equation for  $A$ , viz.,

$$A = -T \int \frac{U}{T^2} dT + IT$$

gives the following expression for  $A$ :

$$A = U_0 + IT - 9R \left( \frac{2.1646}{x^3} - \sum e^{-nx} \left( \frac{1}{n^2x} + \frac{2}{n^3x^2} + \frac{2}{n^4x^3} \right) \right) T$$

In the development, use is made of the relationship

$$\int_x^\infty \frac{e^{-x}}{x^{n+1}} dx = \frac{1}{n} \frac{e^{-x}}{x^n} - \frac{1}{n} \int_x^\infty \frac{e^{-x}}{x^n} dx.$$

By combination of this formula for  $A$  with that for the specific heat, an equation is obtained of the form

$$A = U_0 + IT - 9R \left( \frac{C_v}{36 C_\infty} + \frac{x}{12(e^x - 1)} + \sum \frac{e^{-nx}}{3n} \right) T,$$

which formula is more suitable for calculations. The equation may also be given the compact form

<sup>1</sup> *Sitz. Preuss. Akad., Berlin*, 1160 (1912).

<sup>2</sup> *Ibid.*, 1172 (1912).

$$A = U_0 + IT - 9R \left( \frac{C_v}{36 C_\infty} + \frac{x}{12(e^x - 1)} - \frac{1}{3} C_v (1 - e^{-x}) \right) T,$$

which is identical with the previous one when it is remembered that

$$-\ln(1 - y) = y + \frac{y^2}{2} + \frac{y^3}{3}$$

and

$$y = e^{-x}$$

The formulas employed to represent the specific heats of the several substances are represented in the following table:

Substance.	$C_v$ .
Pb.....	$F(93) + 7.8 \times 10^{-6} T^{3/2}$
Ag.....	$F(216) + 4.8 \times 10^{-6} T^{3/2}$
AgI.....	$F(68.4) + F(215) + 20 \times 10^{-6} T^{3/2}$
PbI <sub>2</sub> .....	$2F(85) + F(129) + 31 \times 10^{-6} T^{3/2}$

$F$  denotes the Debye function,  $F_1$  the older Einstein function, which gives the better run of the curves at the higher temperatures. With the exception of silver iodide the same values were employed by Braune and Koref and interpret fairly accurately the experimental measurement. Their formula for silver iodide was not used since it was found that by its use the experimental data could not be reproduced.<sup>1</sup> The value chosen for silver iodide was that employed by Nernst in his recalculations of Fischer's work.

With these data and with the aid of tables compiled by Nernst and by Pollitzer, the following results were obtained:

$$A_{299} = A_0 + IT_1 - 1789 \text{ calories}$$

$$A_{273} = A_0 + IT_2 - 1624 \text{ calories}$$

The discrepancy between this calculation and that obtained by combining Braune and Koref's values has been traced to the silver iodide values, the values of the latter workers leading to a smaller negative value in calories in the  $A$  and  $U$  curves for the silver iodide-silver-iodine reaction.

Now the difference in magnitude of  $A_{298}$  and  $A_{273}$  can be obtained from the experimental determinations by multiplying the respective temperature coefficients of the two cells by the temperature difference of  $25^\circ$ . Converting to calories this gives in the two cases

$$(a) \quad 0.05 N: \quad 25(-0.000127) \cdot 96500 \cdot 2 \cdot 0.2388 = -146 \text{ cal.}$$

$$(b) \quad 0.10 N: \quad 25(-0.000138) \cdot 96500 \cdot 2 \cdot 0.2388 = -159 \text{ cal.}$$

Consequently the following two relations hold:

<sup>1</sup> It is suggested that the cause of this is probably a typographical error in the  $\beta_v$  values in the original paper. The author has failed to reproduce both specific heat data and the  $A$  and  $U$  calculations of B. and K. with silver iodide although this was readily done in the other case. All the available evidence seems to indicate a typographical error as the cause.

$$(a) \quad -146 = I(298 - 273) - 165$$

$$(b) \quad -159 = I(298 - 273) - 165$$

It is apparent that the two strengths of solution do not give identical figures. To take the mean value is not justifiable until it is shown that there is not a progressive variation in the experimental value with increasing dilution of the solution of potassium iodide. As has been previously stated, reproducible values could not be obtained with an aqueous solution of the two iodides. Even with a 0.02 *N* solution of potassium iodide it has not yet been found possible to obtain results reproducible to less than 5 millivolts, so that for the present the above values must be considered alone. If it were permissible to take the mean, the following equation would be obtained:

$$-153 = I(298 - 273) - 165,$$

so that

$$25 I = 12 \text{ cal.},$$

assuming that the experimental values for the electromotive forces and for the specific heats could be relied upon to one or two calories. On the other hand, if there is a possibility of error in the several determinations amounting to 10 or 20 calories it is obvious that the equation derived above might readily be in agreement with the hypothesis of Nernst and its deduction that  $I = 0$ , the difference being due to experimental error.

Some idea of the experimental error of the specific heat determinations can be obtained. Firstly, as was previously pointed out, there is a divergency between the present calculations and those of Braune and Koref, and this is due to the use by Braune and Koref of a new set of determinations of the specific heats of silver iodide. Their calculations lead to an expression for  $A$  at a temperature of  $20^\circ \text{C}$ .

$$A_{298} = A_0 + IT - 1628 \text{ cal.}$$

With the values employed in the present calculations the corresponding equation is

$$A_{298} = A_0 + IT - 1756 \text{ cal.}$$

It is obvious, therefore, that if one had used the same data as Braune and Koref the difference between the two specific heat terms would have been reduced by nearly 10% or to about 152 calories and that this would have yielded a value intermediate to those obtained experimentally with the two sets of cells for the difference between  $A_{298}$  and  $A_{273}$ .

Secondly, in the present calculations the value of  $\beta\nu$  assumed for lead was 93. The more recent data of Eucken and Schweser<sup>1</sup> at low temperatures point to the value  $\beta\nu = 88$  as more accurate and this is confirmed by the measurements of Kammerlingh Onnes and Keesom<sup>2</sup> at extremely

<sup>1</sup> Eucken and Schweser, *Ber. Akad. Sitzb.*, p. 369 (1914).

<sup>2</sup> *Proc. Amsterdam Acad.*, p. 894 (1914).

low temperatures. If, now, this alteration be made in the calculations as carried out in the present communication, the following equations are obtained:

$$A_{298} = A_0 + IT_1 - 1882$$

$$A_{273} = A_0 + IT_2 - 1701,$$

or a difference in the two specific heats terms of 181 cal., nearly 30 calories greater than the experimental difference between  $A_{298}$  and  $A_{273}$ .

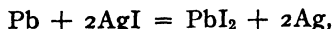
Consequently, for three successive changes in the values for one or other of the specific heat terms the value of  $I$  as calculated by this method has changed successively from 0.5 to 0.0 and then to 1.2. This indicates, with a considerable degree of reliability, the limitations of this particular method of calculating the integration constant. In case the experimental errors of the specific heats are small or in case the cell combination studied possesses a considerable temperature coefficient, the method may be utilized with a fair degree of certainty. When these conditions are not fulfilled great care must be exercised in drawing conclusions from the experimental facts; otherwise, grotesque results may be the outcome. It is evident that, in the present cell combination, even if the integration constant is not equal to zero, its value is considerably smaller than that to which the researches of Jones and Hartmann led in the case of silver iodide alone. This would involve as a consequence that the lead-lead iodide-iodine combination must have a value for the integration constant less than that of the present cell, and, therefore, very probably, a negative value, provided the value for the silver cell be correct.

It is obvious that a considerable increase of experimental evidence relative to the Nernst theorem is eminently desirable. The present investigations have indicated a promising new field of experimental possibilities to which attention is being devoted by the author and for which accurate electrometric and calorimetric determinations as well as the requisite specific heat data are being accumulated.

### Summary.

By an investigation of the cell  $\text{Pb} \mid \text{PbI}_2 \mid N/x \text{ KI} \mid \text{AgI} \mid \text{Ag}$  the thermodynamic relationships of the iodides of silver and lead have been restudied.

It has been shown that the value for the heat of the reaction



as determined by means of the above cell combination agrees satisfactorily with the best calorimetric data for the substances taking part.

The data have been used in an investigation of the assumptions of the Nernst Heat Theorem and of the methods of testing the same. So far as the present experimental evidence relative to specific heats may be employed results favorable to the theorem have been obtained.

In conclusion, I wish to express my indebtedness to Mr. Earle A. Harding for his kind assistance in the preliminary work in connection with this investigation.

PRINCETON, N. J.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY.]

## A STUDY OF THE TENTH-NORMAL HYDROCHLORIC ACID CALOMEL ELECTRODE.<sup>1</sup>

BY N. EDWARD LOOMIS AND MERLE R. MEACHAM.

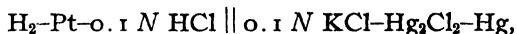
Received August 8, 1916.

### I. Purpose of the Investigation.

The purpose of this investigation was to carefully measure the electromotive force of the system



at 25° with the view of comparing the value so obtained with that of the cell



from which the contact potential has been eliminated. From this comparison the relative potentials of the 0.1 N hydrochloric acid and the 0.1 N potassium chloride calomel electrodes can be determined and thereby the relative degrees of dissociation of the two electrolytes measured.

The degree of dissociation of an electrolyte, as commonly calculated from conductivity data, depends upon the assumption that the mobilities of the ions are independent of the concentration. This assumption was first questioned by Jahn<sup>2</sup> and considerable evidence against it has since been accumulated. The mobility of the hydrogen ion appears to increase with increasing concentration, and consequently the degrees of dissociation of the more concentrated solutions of hydrochloric acid, as determined by conductivity data, are probably too high.

In 1909 Lewis and Sargent<sup>3</sup> assumed that hydrochloric acid and potassium chloride are equally dissociated at equivalent concentrations, even though the apparent dissociation, as indicated by conductivity measurements, is considerably higher for the acid. If the two electrolytes are equally dissociated then the 0.1 N HCl calomel electrode should have the same potential as the 0.1 N KCl calomel electrode. This was assumed to be the case by Lewis and Sargent and their assumption has been adopted by several subsequent workers.

In 1912, however, Lewis<sup>4</sup> showed that the degree of dissociation of 0.1 N

<sup>1</sup> An abstract of this paper was presented at the Urbana meeting of the American Chemical Society.

<sup>2</sup> *Z. physik. Chem.*, 33, 545 (1900); 35, 1 (1900).

<sup>3</sup> *THIS JOURNAL*, 31, 363 (1909).

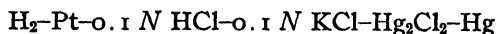
<sup>4</sup> *Idem.*, 34, 1631 (1912).

HCl was in doubt several per cent., and in a later paper<sup>1</sup> he states that, whereas hydrochloric acid and potassium chloride are equally dissociated at 0.01 *N* concentrations, uncertainty exists in regard to the conditions at 0.1 *N*.

It was to throw light upon the uncertainty which has existed in regard to the relative dissociations of 0.1 *N* HCl and 0.1 *N* KCl that this investigation was undertaken.

## II. Previous Work.

The system

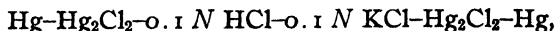


has been carefully studied by several workers. The results which have been obtained at 25°, after correction for the vapor tension of the solution surrounding the hydrogen electrode, and for the new value of the electromotive force of the Weston cell, are summed up in the following table:

Bjerrum <sup>2</sup> .....	0.4273
Loomis and Acree <sup>3</sup> .....	0.4269
Myers and Acree <sup>4</sup> .....	0.4273

Average, 0.4272

This value includes the contact potential existing between 0.1 *N* HCl and 0.1 *N* KCl. Lewis<sup>5</sup> calculates that this potential amounts to —0.0284 volt and as evidence for this value states that Sebastian has obtained for the system



a potential of 0.0284 volt, which represents the contact potential if it is assumed that the two electrolytes are equally dissociated. On the other hand Bjerrum<sup>6</sup> obtains as his best value for the contact potential of the above system —0.0278 and this is just the potential which Myers and Acree obtain by direct comparison of the two electrodes.

It follows then that the difference of potential between the 0.1 *N* HCl hydrogen electrode and the 0.1 *N* KCl calomel electrode lies between 0.3988 and 0.3994 volt, depending upon whether —0.0284 or —0.0278 is adopted for the contact potential. The lower figure 0.3988 is probably nearer the correct value.

At the time this investigation was begun the only figures which were at all reliable for the system



<sup>1</sup> THIS JOURNAL, 36, 1969 (1914).

<sup>2</sup> Z. physik. Chem., 53, 430 (1905).

<sup>3</sup> Am. Chem. J., 46, 585 (1912).

<sup>4</sup> Idem., 50, 396 (1913).

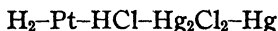
<sup>5</sup> THIS JOURNAL, 36, 1973 (1914).

<sup>6</sup> Z. Elektrochem., 17, 61 (1911).

at 25° had been obtained in the laboratories of Acree and Lewis. Loomis and Acree used only two calomel cells and their value for the electromotive force of the system 0.4004<sup>1</sup> can be considered as only a preliminary measurement. Later Myers and Acree studied this combination more thoroughly and found the difference in potential to be 0.4002.<sup>2</sup>

Lewis<sup>3</sup> states that he has obtained as a mean of several direct comparisons of the 0.1 *N* hydrochloric acid hydrogen electrode with the 0.1 *N* hydrochloric acid calomel electrode, 0.3987 volt, which when corrected for vapor tension and for the new value of the Weston cell becomes 0.3990. He states that more recently Sebastian, working in his laboratory, has obtained the same value. No details of these measurements of Lewis and Sebastian have been published so far as the authors are aware.

Since this investigation was begun there has appeared an article by Ellis<sup>4</sup> in which a careful study of the system



has been made at different temperatures and concentrations. In the course of this study four simultaneous measurements with 0.0999 *N* HCl at 25° gave as a mean 0.39884 volt.

It is evident that the electromotive force of the system



has been in doubt by more than 1.5 millivolts.

### III. Experimental Procedure.

All measurements were carried out at 25° ± 0.01, using much the same apparatus and technique as previously described in the articles of Loomis and Acree. The calomel electrode used in the electromotive force measurements was compared before and after each experiment with the mean of several other calomel electrodes, which were assumed to be of standard potential, and any difference in potential was applied to the measured e. m. f. as a "calomel cell correction." This procedure is even more important in the use of hydrochloric acid calomel electrodes than with potassium chloride calomel electrodes.

Several different types of hydrogen electrodes were used, the most satisfactory form for these experiments being a modification of that described by Frary<sup>5</sup> in which a gauze electrode is substituted for his sheet platinum electrode.

<sup>1</sup> The figure given in the original article is 0.4001. The above value is obtained by correcting for the vapor tension at the hydrogen electrode and for the present value of the Weston cell.

<sup>2</sup> To the value given in the original article 0.399803 is to be applied a correction of 0.0004 for the vapor tension at the hydrogen electrode.

<sup>3</sup> THIS JOURNAL, 36, 1973 (1914).

<sup>4</sup> *Idem.*, 38, 737 (1916).

<sup>5</sup> THIS JOURNAL, 37, 2260 (1915).



The system which was being studied involves only very small contact potentials. The only difference in the solutions upon the two sides of the cell is that the acid at the calomel electrode is saturated with calomel. This would produce only a very small contact potential. Consequently no precautions were taken to insure a fresh plane of contact between the two solutions. Care was always taken however to prevent the contamination of the solution about either electrode by that from the other. This was accomplished by keeping at least one stopcock in the system closed except momentarily during measurements.

All measurements were corrected (a) for variations in the potential of the comparison calomel cell, as already noted; (b) for the barometric pressure reduced to  $0^{\circ}$  and corrected for capillarity and latitude; and (c) for the vapor tension of the solution in the hydrogen electrode chamber. The barometric pressure corrections were calculated by the equation

$$e = -\frac{R.T}{2F} \log_e p = -0.02958 \log_{10} p,$$

in which  $e$  represents the desired correction and  $p$  is the corrected barometric pressure in atmospheres. The correction for the vapor tension of the solution is a constant value and equal to  $+0.00040$  volt.

#### IV. Experimental Results.

The following table summarizes the results of the measurements which were carried out. The first column gives the number of the series. Measurements belonging to the same series were carried out with the same set of calomel cells. The second column gives the experiment number. The third column gives the date of the preparation of the calomel, *viz* the day on which it was set to soaking with the solution with which the calomel electrodes were later filled; the date of filling the calomel electrodes; and the date of measurement of the hydrogen electrode against the calomel electrode. The fourth column gives the measured c. m. f.; the fifth the correction to be applied to the calomel cell; the sixth the correction for the barometric pressure; the seventh the correction for the vapor tension; and the eighth column the final value of the corrected e. m. f.

The fourth series of measurements was brought to a close by the breaking of the comparison calomel electrode. An attempt was made to carry out Series V with only four standard calomel electrodes, but after April 15 the agreement of the electrodes among each other became worse and worse, and the measured differences of potential between the calomel electrodes and the hydrogen electrode became unusually low. It was suspected that the electrodes had become contaminated in some way and for that reason the last few measurements of this series are not included.

Series No.	Expt. No.	Date.		E. M. F. meas.	Meas. E. M. F. Volt.	Cal cell correc. Millivolt.	Barom. correc. Millivolt.	Vap. T. correc. Millivolt.	Final E. M. F. Volt.
		Prep. of calomel.	Prep. of cal. cells.						
I	1	Dec. 20	Jan. 7	Jan. 12	0.39841	-0.16	+0.37	+0.40	0.39902
	2			Jan. 13	0.39877	-0.15	-0.02	+0.40	0.39900
	3			Jan. 14	0.39893	-0.21	-0.07	+0.40	0.39905
II	4	Feb. 21	Feb. 24	Feb. 26	0.39810	±0.00	+0.36	+0.40	0.39886
	5			Feb. 28	0.39824	+0.10	+0.24	+0.40	0.39898
	6			Feb. 28	0.39809	+0.21	+0.26	+0.40	0.39896
	7			Feb. 29	0.39807	+0.28	+0.22	+0.40	0.39897
	*8			Mar. 10	0.39770	+0.90	+0.22	+0.40	0.39922
III	9	Mar. 10	Mar. 13	Mar. 13	0.39761	+0.22	+0.38	+0.40	0.39861
	10			Mar. 14	0.39781	+0.09	+0.29	+0.40	0.39859
	11			Mar. 14	0.39781	+0.17	+0.25	+0.40	0.39863
	12			Mar. 15	0.39832	-0.03	+0.10	+0.40	0.39879
	13			Mar. 16	0.39804	+0.15	+0.10	+0.40	0.39869
	14			Mar. 17	0.39810	+0.12	+0.08	+0.40	0.39870
	15			Mar. 17	0.39809	+0.12	+0.02	+0.40	0.39863
IV	16	Mar. 24	Mar. 27	Mar. 28	0.39805	+0.07	+0.32	+0.40	0.39884
	17			Mar. 29	0.39788	+0.26	+0.20	+0.40	0.39874
	18			Mar. 29	0.39803	+0.10	+0.20	+0.40	0.39873
	19			Mar. 30	0.39817	+0.08	+0.17	+0.40	0.39882
	20			Mar. 31	0.39805	+0.18	+0.22	+0.40	0.39885
	21			Apr. 1	0.39802	+0.15	+0.27	+0.40	0.39884
	22			Apr. 2	0.39819	+0.04	+0.21	+0.40	0.39884
	23			Apr. 3	0.39812	+0.08	+0.27	+0.40	0.39887
	24			Apr. 4	0.39822	+0.13	+0.22	+0.40	0.39897
V	25	Apr. 6	Apr. 11	Apr. 12	0.39797	+0.12	+0.22	+0.40	0.39871
	26			Apr. 13	0.39795	+0.09	+0.26	+0.40	0.39870
	27			Apr. 14	0.39804	-0.02	+0.22	+0.40	0.39864
	28			Apr. 14	0.39809	±0.00	+0.21	+0.40	0.39870
	29			Apr. 15	0.39808	-0.05	+0.22	+0.40	0.39865

Of the twenty-nine measurements recorded in the table, No. 8 is considerably the highest and is omitted from the general average. This measurement was made ten days after the one preceding it and the potentials of the different electrodes had become so discordant that there was much doubt in regard to the proper value of the calomel cell correction. Of the remaining twenty-eight measurements the average value is 0.39879. The individual measurements range from 0.39905 to 0.39859, a total variation of 0.46 millivolt and a maximum variation from the mean of 0.26 millivolt. An instrument correction for the potentiometer reduces the average e. m. f. to 0.39876.

In the five sets of calomel electrodes changes were made in the mercury, calomel, and acid in order to eliminate any error due to possible faulty preparation. The variations in the electromotive force are larger than would seem warranted in the measurement of a system involving only very small contact potentials. The only regularity in these variations which could be detected was a general tendency for the potential of the

calomel electrode to increase upon standing. This would be the result if the solution about the mercury electrode were slow in becoming saturated with calomel. It is not believed that such is the case. Ellis showed in the course of his work that hydrochloric acid calomel electrodes rapidly follow temperature changes, and such could not be the case unless saturation is quickly attained. It seems more probable that some chemical change occurs in the system, probably the change of the calomel to the bichloride as suggested by Clarke, Myers, and Acree.<sup>1</sup> These authors agree with us in regard to the 0.1 *N* hydrochloric acid calomel electrode that "its constancy continues over only a short period of time." Ellis finds that calomel electrodes made up with dilute solutions of hydrochloric acid are less satisfactory than those made up with more concentrated solutions, and that with acid of less than 0.03 *N* concentration are for some reason not at all reliable.

It appears then that the 0.1 *N* hydrochloric acid calomel electrode is not nearly as constant and reproducible as the 0.1 *N* potassium chloride calomel electrode. The age of the electrode is an important factor in determining its potential. This is probably the cause of the great variations in previous measurements of the system



and is the cause of the smaller variations in the measurements which are recorded in this paper.

The average value obtained in the measurement of the hydrogen electrode against the 0.1 *N* hydrochloric acid calomel electrode is 0.39876. We have shown in the earlier part of this article that the most probable value of the potential of the hydrogen electrode against the 0.1 *N* potassium chloride calomel electrode, after allowance has been made for the contact potential, is 0.3988. Within the limits of experimental error we have the same electromotive force in each case, indicating that the 0.1 *N* hydrochloric acid calomel electrode has the same potential as the 0.1 *N* potassium chloride calomel electrode. This in turn implies that hydrochloric acid and potassium chloride are equally dissociated at 0.1 *N* concentration. A difference of 1% in the degree of dissociation of the two electrolytes would cause a difference of 0.3 millivolt in the relative potentials of the two electrodes. It follows from these results therefore that the two electrolytes are not more than 1% different in their degrees of ionization at 0.1 *N* concentration.<sup>2</sup>

<sup>1</sup> *J. Phys. Chem.*, 20, 264 (1916).

<sup>2</sup> Since this paper was placed in the hands of the editors there has appeared an article by Harned (*THIS JOURNAL*, 38, 1986 (1916)) in which he arrives by a different method at the conclusion "that the activity of the ions in 0.1 *M* hydrochloric acid is greater than in 0.1 *M* potassium chloride but only slightly greater. If 0.0730 be ac-

## V. Summary.

### 1. The potential of the system



has been found to be  $0.3988 \pm 0.0002$ .

2. The variations in the electromotive force of this system are probably due to a chemical change in the calomel electrode by which the potential increases with time.

3. This series of experiments indicates that within the limits of experimental error, probably within 1%, hydrochloric acid and potassium chloride are equally dissociated at tenth-normal concentrations.

LAFAYETTE, IND.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY.]

## THE SOLUBILITIES OF LIQUIDS IN LIQUIDS. THE PARTITION OF THE LOWER ALCOHOLS BETWEEN WATER AND COTTONSEED OIL.

BY B. B. WROTH AND E. EMMET REID.

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### Introduction.

According to the commonly accepted partition law a solute C is partitioned between two immiscible solvents, in contact with each other,

$$\frac{C_a}{C_b} = r = \frac{S_a}{S_b}$$

in which  $C_a$  and  $C_b$  are the concentrations of C in the solvents A and B, respectively,  $r$  is a constant ratio, and  $S_a$  and  $S_b$  are the solubilities of the solute in the two solvents. It has frequently been shown that  $r$  is constant only when the solute C exists in the two solvents in the same molecular aggregation. The equality of  $C_a/C_b = r = S_a/S_b$  has been proved for iodine partitioned between water and carbon disulfide, bromoform, and carbon tetrachloride by Jakowkin.<sup>1</sup> His results are as follows:

From solubilities in				From partition experiments.
A.	B.	$S_a$ .	$S_b$ .	
CS <sub>2</sub>	H <sub>2</sub> O	230	+ 0.3387 = 679	685
CHBr <sub>3</sub>	H <sub>2</sub> O	189.55	+ 0.3387 = 559	558.5
CCl <sub>4</sub>	H <sub>2</sub> O	30.33	+ 0.3387 = 89.6	89.7

cepted to represent the ion-activity of the salt, there is reason to assume that the ion-activity of the acid is 0.0755."

A possible explanation of the slight discrepancy between the conclusion of his article and this one may be found in the value which he adopted for the contact potential of 0.1 N HCl-0.1 N KCl. It will be noted that our conclusion is based upon the assumption that this contact potential is -0.0284 volt. If a lower value of this contact potential, such as found by Bjerrum, is correct, then the potential of the calomel electrode toward a solution of 0.1 N KCl is greater than that of a calomel electrode toward a solution of 0.1 N HCl. In other words, if such is the case, 0.1 N HCl is slightly more dissociated than 0.1 N KCl.

<sup>1</sup> *Z. physik. Chem.*, 18, 590 (1895).

Of course, this law holds strictly only in the ideal case where the solvents A and B are absolutely immiscible and neither modifies the solvent power of the other in the slightest. If any appreciable amount of A dissolves in B, the solvent power of B for C is thereby altered and *vice versa*. Steiner<sup>1</sup> and Gordon<sup>2</sup> have shown that the solubilities of gases in water are much altered by the presence of even small quantities of salts in solutions. However, this is not contradicting the partition law, but simply saying that the value of  $S_a$  and of  $S_b$  should be the solubilities of C in A saturated with B and in B saturated with A, rather than the solubilities in the pure solvents.

Jakowkin<sup>3</sup> has also shown that  $r$  changes progressively with the amount of solute C and that the value of  $r$  approaches  $S_a/S_b$  when larger and larger quantities of C are added. When  $C_a$  and  $C_b$  approach zero,  $r$  approaches another limit which is more properly its ideal value, as only when  $C_a$  and  $C_b$  are very small are the solvents A and B unaltered by the presence of C. When larger amounts of C are present A and B become mutually more soluble and the properties of both solvents are altered. In the present work the smallest practicable amounts of C were used.

Assuming  $C_a/C_b = r = S_a/S_b$ , since there are five quantities in this double equation, we may determine any three and calculate the other two. Thus if we measure  $C_a$  and  $C_b$  and thus find  $r$  we need to measure  $S_a$  in order to calculate  $S_b$ .

Such results must, of course, be considered in the light of the above considerations and be accepted with reserve. The present work was undertaken with the aim of applying this to the calculations of solubilities in the case of certain very soluble liquids. The results are considered as suggestive rather than as conclusive. They mean something, but just what they mean may be left for future consideration.

In a series of experiments in which ethyl alcohol was partitioned between cottonseed oil A, and water B,  $r$  was found to be 28.3. The average of a series of experiments gave the solubility of alcohol in the oil,  $S_a$  as 21.1 g. per 100 cc. Calculation gives  $S_b$  as the solubility of the alcohol in 100 cc. water as 600 g. There are many substances of which water dissolves several times its own weight. For instance, 100 cc. of water dissolve 339 g. of cadmium chlorate at 0° and 549 g. at 65°. In these cases, however, though the solubility is great, it is still limited. One hundred grams of water dissolve 907 g. of calcium iodide at 0° but stops there, and if we shake it with 910 g., 3 g. of the salt are left over, while the 100 g. of water dissolve 600 g. of alcohol, but if more alcohol is added it too disappears in the solution.

<sup>1</sup> *Wied. Ann.*, 52, 275 (1894).

<sup>2</sup> *Z. physik. Chem.*, 18, 520 (1895).

<sup>3</sup> *Ibid.*, 18, 590 (1895).

An examination of the phenomena shows that there is an essential difference between a solid solute and a liquid solute in contact with a solvent. The solid solute, except such substances as gelatine, does not absorb or dissolve the solvent, while the liquid solute plays the role of solvent and the result is two solutions. Thus, if dry ether be added to water, the ether which is not dissolved does not remain anhydrous, but dissolves a considerable amount of the water. The figure 600 obtained for the solubility of alcohol in water, is for anhydrous alcohol in contact with its solution in water. If the alcohol were separated from the water by a semipermeable diaphragm, through which the alcohol alone could pass, this condition might possibly be realized.

Such numbers as these, representing a sort of ideal solubilities, are of interest for the comparison of the properties of the members of a series. They have a practical value in the study of extractions.

The lower alcohols have been studied in the hope of being able to arrange them in a series, so as to show the variation of solubility with molecular weight.

It is difficult to find a suitable liquid for the solvent A, since most liquids that are insoluble in water, dissolve too much of the alcohols, Cottonseed oil was chosen on account of its insolubility in water, its non-volatility, and its accessibility. It served the purpose only fairly well since it is rather difficult to handle and gives up a small amount of volatile matter when steam distilled. It mixes with the higher alcohols, so only partition ratios could be determined with these.

Meyer<sup>1</sup> in a study of the influence of temperature upon the partition coefficient has determined the distribution ratio of ethyl alcohol between olive oil and water. His determinations were made at 3° and 30° with the following results:

	G. substance per 100 cc. of		$C_w/C_o$	Mean.
	Water layer.	Oil layer.		
3°	2.69	0.09	29.8	42.7
3°	3.90	0.07	55.7	
30°	2.64	0.14	18.8	21.3
30°	3.82	0.16	23.8	

The wide variation in his results is due to the fact that he determined the alcohol in the oil layer by difference, throwing all the error on the smaller quantity.

His results at 30° approximate those obtained in the present work for the similar cottonseed oil.

### Materials.

**Cottonseed Oil.**—The ordinary oil was purified by distilling with steam for about two hundred hours. When the density of the distillate ap-

<sup>1</sup> *Arch. exp. Path. Pharm.*, 46, 344 (1901).

proached the density of pure water, the oil was assumed to be ready for use. A small amount of alkali in water was added to neutralize and dissolve any free acid, and the oil filtered through a dry paper in a hot water funnel.

Later in the work it was found that Wessen oil required only one day of distilling with steam before being ready for use, and it was then used in the place of the ordinary commercial oil.

**Ethyl Alcohol.**—The ethyl alcohol was refluxed with lime for a period of several days and distilled. It had a density of  $0.78543^{25}/_4$  corresponding to 99.92% alcohol.

**Methyl Alcohol.**—Difficulty was experienced in dehydrating methyl alcohol. It was first refluxed with lime for several days, then with anhydrous copper sulfate, then finally with metallic calcium. Density  $0.79580^{25}/_4$  corresponding to 99.95% alcohol.

**Propyl, Isobutyl and Isoamyl Alcohols.**—All three alcohols were refluxed with metallic calcium for several days and assumed to be practically anhydrous. Their densities were  $0.80715^{25}/_4$ ,  $0.79949^{25}/_4$  and  $0.81225^{25}/_4$ , respectively, not corrected for air displacement.

#### Procedure.

Weighed amounts of oil and water were placed in a 200 cc. glass stoppered bottle. With the lower alcohols several volumes of oil were used to one of water, so as to increase the alcohol in the oil layer. To this mixture a quantity of alcohol, weighed from a pycnometer, was added. A piece of sheet rubber was stretched over the stopper and securely tied around the neck of the bottle. The bottles were then placed in the shaking machine and shaken for one hour in a constant temperature bath at  $25^{\circ}$ . The bottles were completely submerged in the bath during the shaking. It was found that it required three weeks' standing at  $25^{\circ}$  for the layers to separate clear. To obviate this delay, the bottles containing the mixture were centrifuged at 1350 revolutions per minute until the layers became clear. The temperature of the centrifuge was not regulated but was usually not far from  $25^{\circ}$ .

It was found to require about six hours' centrifuging for the ethyl and methyl alcohol mixtures while the propyl, isobutyl and isoamyl required about three hours.

The bottles were then placed in the  $25^{\circ}$  bath until ready for analysis.

**Estimation of Alcohol in Oil Layer.**—The oil layer containing the alcohol was drawn off by means of a special pipet, shaped something like an Ostwald pycnometer. A suitable amount of the oil was weighed out of the pipet into a Kjeldahl flask, out of which it was distilled with steam. The flask was provided with an efficient trap to prevent splashing over. The receiver was provided with a cork having a small opening, and was placed in an ice bath to diminish evaporation.

The alcohol in the weighed distillate was estimated either by the usual density method or by the interferometer. For the interferometer work a table was prepared for each alcohol. Small weighed bulbs were filled with the anhydrous alcohol, sealed and weighed. These bulbs were broken in glass stoppered bottles containing weighed amounts of water. The interferometer readings of a number of these mixtures were plotted against the percentages of the alcohols. From this a table was calculated, which was used in determining the composition of the distillate.

The interferometer readings with weighed mixtures of alcohols and water are given in the following table:

Methyl Alcohol.				Isobutyl Alcohol.			
CH <sub>3</sub> OH %	0.821%	1.50	3.99	C <sub>4</sub> H <sub>9</sub> OH %	1.89%	2.95	3.18 4.21
Reading	0.62	1.08	2.87	Reading	7.31	11.30	12.17 16.40
Reading for 1%	0.75	0.72	0.72	Reading for 1%	3.86	3.82	3.82 3.89
Propyl Alcohol.				Isoamyl Alcohol.			
C <sub>3</sub> H <sub>7</sub> OH %	1.84%	2.67	3.39 4.24	C <sub>5</sub> H <sub>11</sub> OH %	1.42%	2.31	
Reading	5.75	8.57	11.07 14.48	Reading	5.96	9.72	
Reading for 1%	3.12	3.20	3.26 3.41	Reading for 1%	4.19	4.20	

When cottonseed oil is distilled with steam, no matter how long the process is continued, the distillate always contains a small amount of something which changes its density slightly and also gives a reading in the interferometer. The composition of this distillate remains nearly constant for a long time. The densities of the alcoholic distillates were corrected for this by taking densities of distillates obtained with the same lot of oil containing no alcohol. In the interferometer work the steam distillation of the sample of the oil layer was continued for a considerable time after all of the alcohol had passed over. A specimen of the distillate collected at the end of this distillation was used, instead of pure water, in the other cell of the interferometer. Since the interferometer is a differential instrument, the reading thus obtained represented the amount of alcohol present.

A weighed portion of the filtered water layer was distilled in the Kjeldahl flask and the alcohol determined as above.

For the experiments with ethyl alcohol the pycnometer was used and for the other alcohols the interferometer for estimation of the alcohol.

The absolute solubilities of ethyl and methyl alcohol in the oil were found by adding a weighed amount of alcohol to a weighed amount of oil in a small separating funnel. The mixture was then shaken in a constant temperature bath at 25° for two hours.

The funnels were allowed to remain in the bath until the layers became clear. A sample of the oil layer was then drawn off into a Kjeldahl flask and steam distilled, the amount of alcohol being determined as in the above experiments. The funnel was weighed before and after to



get weight of sample. Since alcohol evaporates from this saturated oil solution very readily, much care was taken to effect this transfer with the least possible exposure to the air, but even then it was difficult to obtain concordant results.

Weighed portions of the alcohol layers were evaporated in wide-mouth weighing bottles on a steam bath. The film of oil gained weight on long heating. This materially interfered with the accuracy of the results.

### Results.

The results are given in the table below.

The experiments are given in the order in which they were made and none are omitted except preliminary experiments at beginning of first two series.

In Column 1 is given volume of oil, which was obtained by dividing the weight of oil put in by 0.922, the density of the oil used. In Column 4 is given weight of alcohol for the total oil layer, calculated from the analysis of a weighed portion of the oil layer, while in Column 5 is the amount of alcohol for the total water layer found in the same way. The sums of these amounts of alcohol are given in Column 6. These sums should equal the amounts put in, which are given in Column 3. The amounts found are usually less, indicating loss of alcohol somewhere in the operations. It is likely that most of this alcohol is lost in handling the water layer as this had to be filtered. Excess of alcohol found over that put in may be explained by error in pycnometer estimation or by presence of volatile matter other than alcohol in the distillate. The distillates from the oil layer were usually about 60 cc. so that the total alcohol present amounted to only about 2% in the distillate.

Columns 7 and 8 contain the amounts of alcohol calculated from 100 cc. of oil and water, and the ratio of these is given in Column 9, as the partition ratio for alcohol between oil and water.

As the greatest error seemed to be in the handling of the water layer, the ratios in Column 10 were also calculated, assuming that the values in Column 4 for alcohol in oil layers are correct and estimating the alcohol in water layer by difference, *i. e.*, the difference between the values in Columns 6 and 4. The values calculated in this way are usually higher and are somewhat more regular.

The values of the partition ratios have not been calculated by difference in the case of isobutyl and isoamyl alcohols since the amounts of these alcohols in the two layers are more nearly equal, and the probable errors of estimating the alcohols in the two layers were nearly the same.

Some results which appear erratic are in parentheses and have not been used in making the averages.

### PARTITION OF METHYL ALCOHOL BETWEEN COTTONSEED OIL AND WATER.

[illegible]

### SOLUBILITY OF METHYL ALCOHOL IN COTTONSEED OIL AT 25°.

Wt. Oil sample.	Wt. CH <sub>3</sub> OH found.	Wt. CH <sub>3</sub> OH in 100 g. oil.	Wt. CH <sub>3</sub> OH in 100 cc. oil.
44.36	2.269	5.13	4.73
43.39	2.026	4.67	4.31
42.17	2.420	5.81	5.36
41.47	2.238	5.36	4.95
	Mean,	5.24	4.84

### SOLUBILITY OF COTTONSEED OIL IN METHYL ALCOHOL AT 25°.

Wt. sample.	Wt. oil found.	Wt. oil in 100 g. CH <sub>3</sub> OH.	Wt. oil in 100 cc. CH <sub>3</sub> OH.
7.016	0.0575	8.26	6.57
8.166	0.0701	8.65	6.88
6.7405	0.0513	(7.51)	(5.98)
6.1605	0.0356	(7.45)	(5.93)
11.2777	0.0959	8.57	6.82
13.1285	0.1093	8.32	6.62
		Mean, 8.45	6.74

### PARTITION OF ETHYL ALCOHOL BETWEEN COTTONSEED OIL AND WATER.

[illegible]



### Discussion of Results.

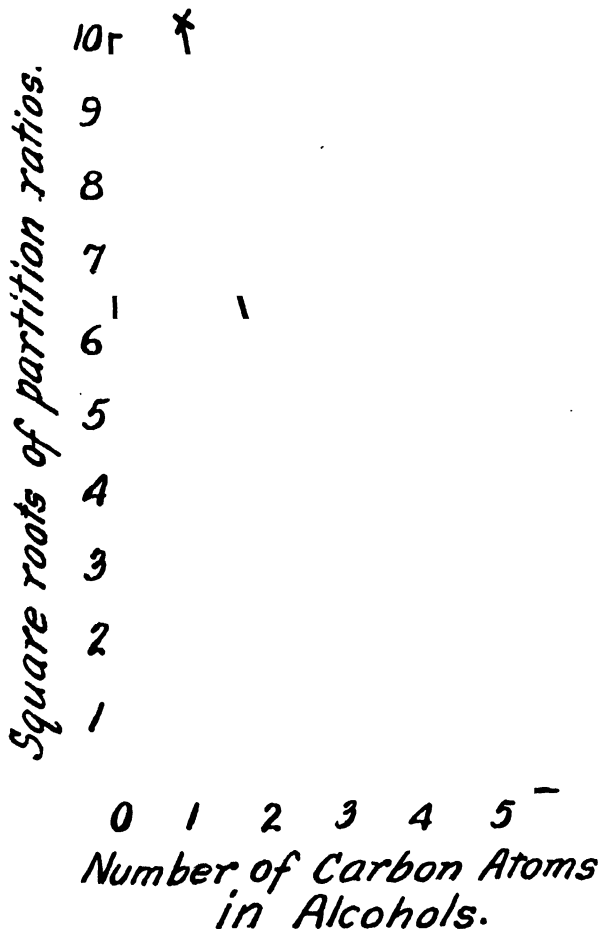
The average results are brought together in table.

PARTITION RATIO BETWEEN WATER AND COTTONSEED OIL.					
Alcohol.	Methyl.	Ethyl.	Propyl.	Isobutyl.	Isoamyl.
Ratio.....	103.6	28.3	6.41	1.70	0.47
Square root of ratio.....	10.18	5.32	2.53	1.30	0.68

The ratios decrease rapidly as the number of carbon atoms in the alcohol increase, each ratio being approximately one-fourth of the preceding ratio.

Taking these ratios as fractions, the numerators which represent the solubilities of the alcohols in water, increase as number of carbon atoms decrease, while the denominators, or the solubilities of the alcohols in the oil increase in the opposite directions. For this reason the square roots of these ratios have been plotted against number of carbon atoms in the

curve below.



The solubility of methyl alcohol in cottonseed oil appears to be 4.84 g. per 100 cc. while for ethyl alcohol it is 21.2 or about four times as great. We have  $4.84 \times 103.6 = 505$  and  $21.2 \times 28.3 = 600$ . From this 505 g. methyl alcohol and 600 g. ethyl alcohol should dissolve in 100 cc. water. These represent, in the same approximation, what may be termed ideal solubilities. At any rate the numbers 4.84 and 103.6 represent something real as determined by experiment and their product must have some meaning also. Further work will have to be done before these results can be satisfactorily inter-

preted. It is surprising that methyl alcohol gives the smaller number 505, while ethyl alcohol gives the larger number 600. It was expected that methyl alcohol would give the larger number as the fact that methyl alcohol is more difficult to salt out of a solution than ethyl, seems to indicate a greater affinity for water and, hence a greater solubility in water. The difficulty may be in the numbers 4.84 and 21.2, the directly determined solubilities of the two alcohols in the oil. These do not represent the amounts of alcohol taken up by the oil when in contact with the pure alcohols, but the amounts in the oil when the oil is in contact with solutions of the oil in the two alcohols. If we consider molecular solubilities, the order is what we should expect, since  $505 \div 32 = 15.8$  and  $600 \div 46 = 13.0$ .<sup>1</sup> Taking the higher and more concordant values we find that 100 g. of methyl alcohol dissolve 8.45 g. of cottonseed oil and 100 g. ethyl alcohol, 11.75 g.

Experiments showed that propyl, isobutyl, and isoamyl alcohols mix with cottonseed oil in all proportions. This prevented the determinations of their direct solubilities. The solubilities of isobutyl and isoamyl alcohols in 100 cc. water are given in the tables as 9.55<sup>18°</sup> and 2.67<sup>22°</sup>. According to the above reasoning, the solubilities of these two alcohols in the oil should be  $9.55 \div 1.70 = 5.6$  and  $2.67 \div 0.47 = 5.6$ . This shows that we must be guarded in drawing conclusions and that there are factors which are not taken into consideration in the reasoning as stated above.

These alcohols, when they contain a few per cent. of water, do not mix with the oil. The phenomena of mutual solubility are quite complex and require much further study. This work is being continued in this laboratory.

### Summary.

1. The partition ratios of methyl, ethyl, propyl, isobutyl and isoamyl alcohols between water and cottonseed oil at 25° are found to be 103.6, 28.3, 6.41, 1.70 and 0.47, respectively.
2. These are found to change regularly with increased number of carbon atoms.
3. The solubilities of methyl and ethyl alcohols in cottonseed oil are 4.84 and 21.2 g. per 100 cc. oil.
4. The attempt has been made by using these numbers and the partition law to calculate the ideal solubilities of the lower alcohols in water.

BALTIMORE, MD.

<sup>1</sup> Suggestion of Associate Editor.

[CONTRIBUTIONS FROM THE BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.]

## THE SEPARATION OF LITHIUM FROM THE OTHER ALKALI METALS.

By SAMUEL PALKIN.

Received August 5, 1916.

Numerous methods for the separation of lithium from the other alkali metals have been proposed, and in a paper by Skinner and Collins<sup>1</sup> these methods are carefully reviewed. Inasmuch as the errors and difficulties involved in each case have been so clearly pointed out by the above mentioned investigators, no attempt will be made in this paper to review fully the literature on the subject, except to mention those instances where the work has a direct bearing on the principles involved in the method herein proposed.

In brief, it may be stated that the methods depending on organic solvents for the extraction of lithium are of two classes: (1) Those in which the dried mixed chlorides are treated with the solvent. The Rammelsberg<sup>2</sup> (ether-alcohol) method, the Kahlenberg-Krauskopf<sup>3</sup> (pyridine) method and the Winkler<sup>4</sup> (isobutyl alcohol) method are of this class. (2) Those in which the sodium and potassium chlorides are precipitated from solution by the organic solvent. This is the case with the Gooch<sup>5</sup> (amyl alcohol) method.

The salient objections to the methods of the first class, as pointed out in the paper of Skinner and Collins, are (1) tendency to occlusion, therefore incomplete extraction of the lithium; (2) possibility of solution of some of the sodium and potassium chlorides in the lithium solvent; (3) formation of lithium hydroxide on drying the chlorides (the hydroxide being insoluble in the organic medium).

The objections to the methods of the second class, which hitherto has been limited to that of Gooch, are as follows: (1) The amyl alcohol dissolves some of the other salts (sodium and potassium chlorides) and a correction must therefore be applied. The separation is consequently not absolute. (2) The unpleasant odor and disagreeable physiological action of its vapors make it quite objectionable to work with.

The method proposed in this paper, like the Rammelsberg<sup>2</sup> method, makes use of alcohol and ether but in a totally different manner. Instead of *dissolving* out the lithium chloride, the sodium and potassium chlorides are progressively *precipitated* from a water solution. The es-

<sup>1</sup> U. S. Dept. Agr., Bur. Chem., *Bull.* 153 (1912).

<sup>2</sup> *Pogg. Ann.*, 66, 79 (1845).

<sup>3</sup> *THIS JOURNAL*, 30, 1104 (1908).

<sup>4</sup> *Z. anal. Chem.*, 52, 628-40 (1913).

<sup>5</sup> *Am. Chem. J.*, 9, 33-51 (1887).

<sup>6</sup> *Loc. cit.*

entials of the method are as follows: The dried mixed chlorides are dissolved in a definite minimum amount of water acidified with HCl, and the major portion of the sodium and potassium chlorides is precipitated by the addition of absolute alcohol followed by ether. The mixture is then filtered, the filtrate evaporated and the residue taken up in absolute alcohol containing a drop of HCl. The residual amount of sodium and potassium chlorides, which under the conditions prescribed rarely exceeds 0.006 g., is then precipitated completely by addition of ether. It will therefore be seen that the objections to the existing methods, as enumerated above, are eliminated in the proposed method.

### Experimental.

In order to determine the relative solubility of sodium and potassium chlorides in mixtures of alcohol and ether containing water and hydrochloric acid, a large number of experiments were performed, with a view of obtaining the optimum proportions for the precipitation of these salts. The few following experiments will serve as illustrations:

TABLE I.  
Relative Solubilities of Sodium and Potassium Chlorides.

	1.	2.	3.	4.	5.	7.	8.
NaCl (g.).....	0.1500	0.1500	0.1500	0.1500	0.0500	....	0.1000
KCl (g.).....	0.1500	0.1500	0.1500	0.1500	0.0500	0.1000	....
H <sub>2</sub> O (cc.).....	6	6	0	0	0	0	0
Conc. HCl (cc.)....	2	2	0.3	0.3	0.3	0.3	0.3
Abs. alcohol (cc.)...	80 <sup>1</sup>	80	60	60	60	60	60
Ether <sup>2</sup> .....	240	240	300	300	300	300	300
Salt recovered (g.)..	0.2702	0.2904	0.2992	0.2993	0.0995	0.0995	0.0996
Salt dissolved (g.)...	0.0298	0.0096	0.0008	0.0007	0.0005	0.0005	0.0004
Salt dissolved g. per							
100 cc. solvent....	0.0091	0.003	0.0002—	0.0002—	0.00011	0.0001+	0.0001+

The experiments on the separate salts, sodium chloride and potassium chloride, respectively, show that only about 0.0005 g. remains in solution in a volume of 360 cc. of liquid. Since only about one-sixth of this volume is used in the final precipitation, the loss is negligible. Experiments on the mixed sodium and potassium chlorides show only a very slightly greater amount dissolved (less than 0.0008 g. per 360 cc.), which is negligible for the volumes used in the actual determinations. Numerous subsequent experiments (Table IV), where separation of lithium from the other alkali metals have been carried out, show quite clearly that the weights of sodium and potassium chlorides recovered are, within experimental errors, practically those used.

<sup>1</sup> In Expt. 1 95% alcohol was used. The remaining ones were carried out with absolute alcohol.

<sup>2</sup> The ether used in these and following experiments was U. S. P., sp. gr. 0.716–0.717 at 25°.

The presence of a large excess of hydrochloric acid was found unnecessary. A slight acidity, however, was found quite essential for the complete aggregation and precipitation of the sodium and potassium chlorides, as illustrated by the following experiments:

TABLE II.  
Effect of HCl on Precipitation of Sodium and Potassium Chlorides.

	1.	2.	3. <sup>1</sup>	4.	5.
Mixed salt NaCl and KCl.....	Excess	Excess	Excess	Excess	Excess
Water.....	0	0	0	0	0
Conc. HCl (cc.).....	0	0.05	0	0.10	0.30
Abs. alcohol (cc.).....	20	20	20	20	60
Ether (cc.).....	100	100	100	100	300
Salts dissolved per 100 cc. of liquid....	0.0012	Not weigh- able	..	0.0003	0.0006
Condition of filtrate.....	Turbid	Clear	Turbid	Clear	Clear

The lithium chloride used was prepared from lithium carbonate by treatment with hydrochloric acid. The lithium carbonate available was found to contain a considerable amount of sodium and potassium salts. The purification of the chloride from the other alkali metals was carried out by the method of separation described in this paper and the resulting residue from the alcohol-ether solution evaporated; gently ignited and powdered. This powder was then tested for purity in the following manner: (a) 1 g. dissolved completely without residue in 20 cc. C. P. pyridine on heating. The pyridine had been previously purified by distillation over KOH, the fraction boiling at  $115+^{\circ}$  being used. (b) 1 g. dissolved completely in 10 cc. absolute alcohol + 1 drop concentrated HCl + 50 cc. ether. No precipitate formed after two hours.

A number of experiments were performed to test the extent of solubility of lithium chloride in varying mixtures of alcohol and ether containing hydrochloric acid. It was found that approximately 10.5 g. were dissolved by 580 cc. of a mixture of one part absolute alcohol and three parts ether at room temperature (about  $24^{\circ}$ ), and that 1 g. of lithium chloride dissolved quite readily in 10 cc. absolute alcohol + 1 drop concentrated HCl, and remained in solution when five times its volume (50 cc.) of ether was added.

Experiments in Table III show the amounts of sodium and potassium chlorides retained in solution after the first precipitation, under the conditions given in the proposed method. The maximum quantity seems to be about 0.006 g. The exact quantity, however, is quite immaterial, as it is all removed in the second or final precipitation. Table IV shows results obtained with mixtures of all three salts, sodium, potassium and

<sup>1</sup> 0.1 cc. HCl was added to No. 3 and allowed to stand  $\frac{1}{2}$  hour and the solution became clear.



lithium chlorides. The sodium and potassium chlorides were prepared by precipitating each from a saturated solution with concentrated hydrochloric acid and heating the precipitate to dull redness. A mixture was prepared consisting of 50% sodium chloride and 50% potassium chloride.

TABLE III.—RESULTS ON ONE PRECIPITATION.

	1.	2.	3.	4.	5.	6.	
NaCl + KCl used (g.).....	0.4950	0.4900	0.4500	0.4000	0.3000	0.0500	·
NaCl + KCl found.....	0.4898	0.4856	0.4460	0.3944	0.2958	0.0440	
Li <sub>2</sub> SO <sub>4</sub> found.....	0.0110	0.0181	0.0683	0.1332	Spattered		
Li <sub>2</sub> SO <sub>4</sub> calc.....	0.0064	0.0127	0.0637	0.1274			
	7.	8.	9.	10.	11.	12.	13.
NaCl + KCl used (g.).....	0.8500	0.8500	1.0000	1.0000	0.7500	1.0000	0.7500
NaCl + KCl found.....	0.8466	0.8469	0.9957	0.9930	0.7426	0.9985	0.7494
Li <sub>2</sub> SO <sub>4</sub> found.....	Recorded in Table IV.						

TABLE IV.—RESULTS OBTAINED BY APPLICATION OF PROPOSED METHOD.

	1.	2.	3.	4.	5.	6.	7.
NaCl, KCl used (g.)..	0.2500	0.4950	0.4900	0.4500	0.4000	0.0100	0.4900
NaCl, KCl found....	0.2499	0.4954	0.4906	0.4500	0.3997	0.0101	0.4897
Li <sub>2</sub> SO <sub>4</sub> .....	0.3177	0.0071	dish				
			crkd.		0.0640	0.1258	0.6236
LiCl equiv.....	0.2452	0.0054		0.0494	0.0971	0.4812	0.0097
LiCl calc.....	0.2451	0.0049	0.0098	0.0490	0.0980	0.4806	0.0098
	8	9.	10.	11.	12.	13.	14.
NaCl, KCl used (g.)..	0.4000	0.3000	0.0100	0.2500	0.4000	1.0000 <sup>1</sup>	0.7500 <sup>2</sup>
						NaCl	NaCl
NaCl, KCl found....	0.3994	0.3002	0.0102	0.2500	0.4004	1.0004	0.7496
Li <sub>2</sub> SO <sub>4</sub> .....	0.1269	0.2547	0.6367	Spattered		0.0064	0.1538
LiCl equiv.....	0.0979	0.1966	0.4914	..	..	0.0049	0.1187
LiCl calc.....	0.0980	0.1961	0.4902	..	..	0.0047	0.1182
	15.	16.	17.	18.	19.	20.	21.
NaCl, KCl used (g.)..	1.0000 <sup>3</sup>	0.7500 <sup>4</sup>	0.4000	0.3750	0.8500	0.5000	0.5000
	KCl	KCl					
NaCl, KCl found....	0.9996	0.7497	0.3996	0.3752	0.8501	0.5006	0.5000
Li <sub>2</sub> SO <sub>4</sub> .....	0.0065	0.1534	..	..	..	..	..
LiCl equiv.....	0.0050	0.1184	0.0941	0.1183	0.1200	..	0.0012
LiCl calc.....	0.0047	0.1182	0.0944	0.1182 0.1175	} ..		0.0009
AgCl = LiCl.....	..	..	0.3182	0.4002	0.4055	Spilled	
	22.	23.	24.	25.	26.	27.	
NaCl, KCl used (g.)..	0.5000	0.5000	0.8500	1.0000	0.0100	0.2500	
NaCl, KCl found....	Crucible spilled		0.5002	0.8504	1.0000	0.0095	0.2496
Li <sub>2</sub> SO <sub>4</sub> .....	..	..	..	..	0.0129	0.3173	
LiCl equiv.....	0.0021	0.0050	0.1203	0.0049	0.0100	0.2449	
LiCl calc.....	0.0018	0.0045	..	..	0.0098	0.2452	
AgCl = LiCl.....	0.0072	0.0174	0.4058	0.0165			

<sup>1</sup> NaCl only.    <sup>2</sup> NaCl only.    <sup>3</sup> KCl only.    <sup>4</sup> KCl only.

TABLE V.

		E. K. Nelson.		H. E. Buchbinder.		E. C. Merrill.	
		Taken, g.	Found, g.	Taken, g.	Found, g.	Taken, g.	Found, g.
1.....	KCl, NaCl	0.4941	0.4939	0.5000	0.4993	0.2504	0.2502
	LiCl	0.0047	0.0053	0.0039	0.0046	0.2452	0.2466
2.....	KCl, NaCl	0.3538	0.3539	0.2000	0.1999	0.0065	0.0063
	LiCl	0.1180	0.1177	0.1968	0.1965	0.4910	0.4897
3.....	KCl, NaCl	0.0614	0.0623	0.0100	0.0104	..	..
	LiCl	0.3540	0.3534	0.3936	0.3930	..	..

The lithium chloride (purified as described previously) was used in the form of an alcoholic solution in nearly all the experiments, except in those few cases where large quantities of lithium were necessary, when the quantities were weighed. The alcoholic solutions were made up to volume (about 2.5 g. in 500 cc.) at definite temperature (about 24°) and aliquot portions were measured by a pipet at the same temperature, both for the blank determinations and actual experiments, delivered into Erlenmeyer flasks or tall beakers and evaporated to dryness on the steam bath. Weighed quantities of the other salts were then added. The results in Table IV are self-explanatory. The lithium was weighed in most cases as the sulfate, although in a number of instances it was determined by the "optional method for lithium" as described in the proposed method, that is, by precipitating the halogen as a silver salt after titrating the excess of HCl with 0.1 *N* alkali and calculating the lithium chloride therefrom.

Some difficulty was experienced in converting large quantities of lithium chloride into  $\text{Li}_2\text{SO}_4$  and bringing it to a constant weight. A high temperature was necessary. With large quantities of lithium there was some tendency to spatter.

An experiment was made to determine the amount of sodium and potassium chlorides dissolved by the ether-alcohol mixture used in washing. A Gooch crucible containing about 0.5 g. of the mixed salts was ignited, cooled and weighed. This was then washed with 120 cc. of the ether-alcohol mixture (1 part 95% alcohol and 4 parts ether) as directed in the proposed method. The crucible on drying, igniting and weighing showed no change in weight. No residue was found on evaporation of the filtrate.

The method was submitted to three coöperators, Messrs. E. K. Nelson, H. E. Buchbinder and E. C. Merrill, of the Bureau of Chemistry. Definite amounts of lithium were taken in the form of solution, the lithium content of which was previously determined. The mixed sodium and potassium chlorides were, in each case, weighed out by the coöperators. The following results were obtained by them, the lithium being weighed as sulfate.

### The Proposed Method.

The total alkali chlorides are dissolved in a minimum amount of cold water in a tall 200 cc. beaker. About 1.5 cc. will be more than sufficient for 0.5 g. of the salts. One drop of concentrated HCl is added and *gradually* 20 cc. absolute alcohol—the alcohol being dropped into the center of the beaker (not on the sides) while rotating. The sodium and potassium chlorides should be precipitated in a perfectly uniform granular condition. In a similar manner while rotating the beaker, 60 cc. ether are added and the mixture is allowed to stand about 5 minutes, or until the precipitate is well agglomerated and the supernatant liquid almost clear. The beaker is rotated occasionally.

The mixture is then filtered through a weighed Gooch crucible into an Erlenmeyer flask, using a bell-jar arrangement. The beaker is thoroughly washed with a mixture of 1 part alcohol and 4 to 5 parts ether. A rubber tipped rod is necessary for this purpose. The precipitate in the Gooch crucible is also well washed and the crucible set aside. The funnel is well washed in order to remove any lithium therefrom into the flask containing the filtrate.

The filtrate is evaporated to dryness on the steam bath (using a current of air). The residue is taken up with 10 cc. of *absolute alcohol*, warming if necessary, so that practically everything passes into solution. If a slight film remains on the bottom of the flask and sides, it is removed by rubbing with a rubber-tipped glass rod. While rotating the flask, 50 cc. ether are added. *One drop* of concentrated HCl is added, the flask rotated and allowed to stand for one-half hour. It is well to rotate the flask at frequent intervals. When the fine precipitate has agglomerated (only a very small amount is usually precipitated), it is filtered through the same crucible as used in the first precipitation, into a tall beaker. The residue is washed with ether-alcohol mixture, using the same precautions as outlined in the first precipitation. After drying in an oven, the crucible is gently ignited, cooled and weighed.

The ether-alcohol solution of lithium is evaporated on the steam bath. The residue is taken up in a little water and a slight excess of sulfuric acid added. The solution is then carefully transferred to a weighed porcelain or platinum dish. The solution is evaporated as far as possible on the steam bath and the residue is then very gently ignited over a flame. By placing the dish on a triangle over an asbestos gauze and using a low flame, the solution can be evaporated without spattering.

The residue is then carefully ignited over a full flame. When charring has occurred, it is well to repeat the ignition with sulfuric acid. The factor used for conversion of lithium sulfate to lithium chloride was 0.7718.<sup>1</sup>

<sup>1</sup> With the 1916 atomic weights this factor becomes 0.7713, which does not however materially influence the results.

### Optional Method for Lithium.

The solution of the lithium in the ether-alcohol is evaporated to dryness on a steam bath and finally dried in an oven at  $110^{\circ}\text{C}$ . for 15–20 minutes. The residue is taken up in 5–10 cc. alcohol, warming if necessary. This solution is diluted with about 50 cc. of water. If a slight sediment remains, the liquid is filtered through a Gooch crucible and washed with water. A few drops of phenolphthalein are added to the filtrate (the reaction should be acid) and the liquid titrated with tenth-normal alkali. The chlorides are precipitated as the silver salt and from the weight of the latter there is subtracted the amount corresponding to the hydrochloric acid determined in the titration. The factor used for converting  $\text{AgCl}$  into  $\text{LiCl}$  was 0.2958.

Where the total quantity of mixed chlorides is greater than 0.5 g., proportionately larger quantities of solvents are necessary in the first precipitation. The second precipitation is carried out in exactly the same manner as for 0.5 g. of salts indicated in the method. More accurate results have been obtained, however, with quantities of total chlorides not exceeding 0.5 g.

WASHINGTON, D. C.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

## THE PURIFICATION AND ATOMIC WEIGHT OF YTTRIUM.

[SECOND PAPER.]

BY B. SMITH HOPKINS AND CLARENCE W. BALKE.

Received September 15, 1916.

A preliminary paper on this subject by Egan and Balke appeared in THIS JOURNAL in April, 1913, in which the sources of material, the preliminary processes of purification and the trial determinations of the atomic weight were discussed. Since the publication of this paper, the work has progressed steadily and the purpose of the present communication is to report progress on the problem.

### Historical.

The atomic weight of yttrium has been determined by a large number of investigators. The results obtained previous to 1873 are of little value since the material used certainly contained considerable quantities of rare earths other than yttrium. Some of these early investigators, however, obtained numbers which are surprisingly close to the accepted value.

In 1873 Cleve and Höglund<sup>1</sup> published a memoir in which six determinations of the ratio  $\text{Y}_2\text{O}_3$  to  $\text{Y}_2(\text{SO}_4)_3$  are recorded, the mean value obtained being 89.58. The material used in this series was known to contain a small amount of terbium, which the authors attempted in vain to remove

<sup>1</sup> K. Svenska Vet. Akad. Handlingar, Bb. 1, No. 8 (1873).

by the slight solubility of terbium formate and double potassium sulfate. Nine years later Cleve published another paper<sup>1</sup> in which he described the further purification of his material. The small amount of terbium was removed by fractional precipitation of the nitrate with oxalic acid. By this means four fractions of constant molecular weight were obtained, and with this material twelve determinations of the atomic weight of yttrium were made by observing the gain in weight when the dry oxide, was converted to anhydrous sulfate. The average value obtained in this second series was 89.12.

Jones<sup>2</sup> determined the atomic weight of yttrium in 1894, using material prepared by Professor Rowland, who used the method of fractional precipitation with potassium ferrocyanide. This material was estimated, by examination of its spectrum, to contain less than 0.5% of other elements. Two series of ten determinations each were made; in one the oxide was dissolved in sulfuric acid and the excess acid expelled by heating; in the other the crystallized sulfate was ignited to the oxide with the blast lamp. The results obtained were 88.96 for the first series and 88.98 for the second. These results were criticised by Delafontaine,<sup>3</sup> but Jones' reply<sup>4</sup> was insistent and his results practically determined the international value until recently.

In 1900 Muthmann and Böhm published<sup>5</sup> the result of a single determination, in which the sulfate was ignited to the oxide, obtaining the value 88.97, which agrees exactly with that obtained by Jones.

In 1901 G. and E. Urbain<sup>6</sup> in discussing the purification of yttrium material, stated that a final fraction gave an atomic weight of 88.6, but no information is supplied concerning the method used or the purity of the material.

In the same year Bodman<sup>7</sup> published the results of three determinations, obtaining the value 91.57 from the transformation of the oxide to the sulfate.

K. T. Postius, in his dissertation presented to the Technische Hochschule at Munich in 1902, describes seven determinations of the ratio  $Y_2O_3 : Y_2(SO_4)_3$  with an average value of 88.35. In expelling the excess acid from the sulfate he used temperatures from 350° to 370° only.

Buill<sup>8</sup> in 1905 obtained the value 89.70 from two determinations of

<sup>1</sup> *K. Svenska Vet. Akad. Handl.*, No. 9 (1882); *Compt. rend.*, 95, 1225 (1882); *Bull. soc. chim.*, 39, 120 (1883).

<sup>2</sup> *Am. Chem. J.*, 17, 154 (1895).

<sup>3</sup> *Chem. News*, 71, 243 (1895).

<sup>4</sup> *Ibid.*, 71, 305 (1895).

<sup>5</sup> *Ber.*, 33, 42 (1900).

<sup>6</sup> *Compt. rend.*, 132, 136 (1901).

<sup>7</sup> *Bihang. Svensk. Vet. Akad. Handl.*, [2] 26, No. 3 (1901).

<sup>8</sup> *Z. anorg. Chem.*, 47, 464 (1905).

the same ratio, making use of the microbalance. In this paper there is also an interesting study of the effect of heating yttrium sulfate in an electric furnace for 15-minute periods. He found that the neutral sulfate when heated for this length of time was stable between the temperatures of  $450^{\circ}$  and  $650^{\circ}$ ; that the material was completely transformed into the basic salt corresponding to the formula  $Y_2O_3 \cdot SO_3$  at  $900$ – $950^{\circ}$ ; and that above these temperatures the material began to break down into the oxide, the decomposition becoming complete at  $1100^{\circ}$ .

Feit and Przibylla<sup>1</sup> departed from the usual method of determining the atomic weight of yttrium by using a titration method. The oxide was dissolved in an excess of 0.5 *N* sulfuric acid and the excess acid titrated with 0.1 *N* sodium hydroxide, using methyl orange as an indicator. The proportion of oxygen in the oxide and in turn the atomic weight of yttrium were calculated from the data obtained. The average of their six determinations gave yttrium an atomic weight of 89.35.

A. Bettendorff<sup>2</sup> in 1907 obtained yttria of a high degree of purity by fractional precipitation with potassium ferrocyanide. His purest fraction was shown by spectrographic study to be free from other rare earths. A single determination, the details of which are not given, showed his product to have an atomic weight of 88.76.

In 1913 Meyer and Wuorinen<sup>3</sup> discussed at length the results obtained by various investigators and compared several of the methods used in obtaining pure yttria. By using a combination of methods they prepared a product of a high degree of purity with which the atomic weight was determined by the synthesis of the sulfate. The authors found that the excess of sulfuric acid could not be expelled even at a temperature of  $500^{\circ}$ . Instead of trying to drive off the excess acid they proceeded as follows: The weighed oxide was dissolved in a small excess of sulfuric acid; the solution was evaporated to dryness; the sulfate was then heated to a temperature of  $450^{\circ}$  to  $500^{\circ}$  and weighed; finally the amount of acid retained by the salt was determined by titration with decinormal sodium hydroxide, using methyl orange as an indicator. The acidity determined in this way was calculated as  $SO_3$  and subtracted from the weight of the yttrium sulfate, giving a corrected weight from which the atomic weight was determined. Two determinations were made, giving an average of 88.6.

**The Ratio.**—A review of the methods which have been used in determining the atomic weight of yttrium shows that the sulfate was used in some manner in every case, and that in the majority of investigations the synthesis of the sulfate was relied upon to give the desired ratio. In two

<sup>1</sup> *Z. anorg. Chem.*, **50**, 262 (1906).

<sup>2</sup> *Ann.*, **352**, 88 (1907).

<sup>3</sup> *Z. anorg. Chem.*, **80**, 7 (1913).

cases the values were based upon the decomposition of the sulfate, and in two others they depended upon titration methods. A comparison of the values obtained from the synthesis of the sulfate shows that Bodman's value, 91.57, is the highest, and Postius', 88.35, the lowest. It is perhaps worthy of note also that these two investigations were nearly or quite contemporaneous. It would seem that the difference in the results is much too great to be accounted for wholly by the varying purity of the material used, since if Postius' results are correct then Bodman's product must have contained about 6.5% of erbia or an equivalent amount of other rare earths. This quantity would certainly be detected by the means used in proving the purity of the material and it would seem that this wide variation must be explained in some other way than by differences in the purity of the material employed.

After repeated efforts to obtain concordant results with the sulfate method, we are led to the conclusion that the method is not ideal for three reasons. First, the anhydrous sulfates are extremely hygroscopic and Nilson has shown that they cannot be weighed in a perfectly anhydrous condition if removed from a phosphorus pentoxide desiccator of the ordinary type, and Bunsen declares that a thin glass weighing tube is not sufficient to protect the sulfates from the moisture of the air. It seems that all investigators have not had this point in mind in their manipulation. A second difficulty with the sulfate method as generally carried out, is the impossibility of telling when the excess sulfuric acid has been expelled. It is customary to follow the method suggested by Cleve and heat to constant weight and then if the residue dissolves to a clear solution to consider that only the normal anhydrous sulfate remained. It is obvious that this test is a good one to discover when the heating is carried too far and too much  $\text{SO}_3$  has been expelled, but it is of no value in determining when some acid still remains in the sulfate. If the heat is applied suddenly, as with a flame, we would expect the center of the mass to remain acid for some time after the outer layer had become neutral or basic. Brauner and Pavlicek,<sup>1</sup> in a similar study of the effect of heating lanthanum sulfate, state that in 27 experiments not a single case was discovered in which the mass was homogeneous, the tendency being for the outer layers to become basic, the middle portions neutral, and the central upper layers acid. When such a mass is dissolved in water two facts should be noted: (1) a clear solution may be obtained but its reaction to indicators is a matter of chance; (2) a portion of the mass which is basic should dissolve more slowly than the rest and this experience was noted by Jones<sup>2</sup> who explained the phenomenon by supposing that a hydrate of lower solubility had been formed. We have had a similar ex-

<sup>1</sup> *Trans. Chem. Soc.*, 81, 1243 (1902).

<sup>2</sup> *Am. Chem. J.*, 17, 160 (1895).

perience with nearly every sample of heated sulfate which has been dissolved in water and we are led to believe that the less soluble portion is the basic outer layer which finally dissolves in the acid from the inner portions.

A third reason for questioning the accuracy of the sulfate method comes from the fact that it is impossible to obtain constant weight except at some definite temperature. As long ago as 1887 Bailey showed<sup>1</sup> that on heating "didymium" sulfate containing some free sulfuric acid up to and above 360°, no equilibrium could be obtained, but each increase in temperature is followed by a further loss in weight. Brauner and Pavlicek<sup>2</sup> reported the same experience with lanthanum sulfate, and showed that a temperature of 600° or more is needed to expel all the acid. Brill claims<sup>3</sup> that normal yttrium sulfate is stable between the temperatures of 450° and 650°. It is to be noted, however, that Brill heated his material for 15-minute periods only. In order to discover whether or not the sulfate would continue to remain constant in weight if kept for long periods at a definite temperature we have performed two tests. Two samples of the oxide from different sources were weighed out in platinum crucibles and converted into the sulfate in the usual manner.<sup>4</sup> These sulfates were then heated in an electric muffle, the temperature being determined by a recently calibrated pyrometer. At the end of the heating periods the hot crucibles were placed in weighing bottles whose stoppers were apparently tight, and the bottles put in a roomy sulfuric acid desiccator. When cold the stoppers of the bottles were opened for a moment and the bottles containing the crucibles weighed by substitution, the tare being a similar bottle containing an empty platinum crucible which was treated exactly like the crucibles containing the sulfates. The results are given in the following table, the weights being the values obtained in air:

TABLE I.

No.	Temp.	Hours.	Crucible I.		Crucible II.	
			Sulfate.	Atomic weight.	Sulfate.	Atomic weight.
1	470°	4	0.73574	91.97	0.78520	91.41
2	470°	16	0.73503	92.19	0.78486	91.51
3	485°	14	0.73503	92.19	0.78461	91.58
4	525°	12	0.73358	92.64	0.78477	91.54
5	575°	6	0.73382	92.56	0.78450	91.62
6	580°	7	0.73341	92.69	0.78442	91.64

These results show that there is generally a loss in weight when the sulfates are heated for long periods. The cases in which there is a gain in weight are probably due to the absorption of moisture by the hygroscopic

<sup>1</sup> *Trans. Chem. Soc.*, 51, 683 (1887).

<sup>2</sup> *Ibid.*, 81, 1250 (1902).

<sup>3</sup> *Z. anorg. Chem.*, 47, 464 (1905).

<sup>4</sup> *THIS JOURNAL*, 35, 370 (1913).



sulfate. The sulfates from both crucibles were dissolved in water and showed some basic salts present, hence the gradual loss in weight was not due at all stages to the giving off of occluded sulfuric acid, but to the loss of  $\text{SO}_3$  from the yttrium sulfate. It is difficult to say just where the heating should have been discontinued in order to give the normal salt and the true atomic weight.

On account of the divergent results and the unreliability of the ratio depending on the synthesis of the sulfate, it seems highly desirable that some entirely different ratio should be used. Encouraged by the early results obtained with the ratio  $\text{Y}_2\text{O}_3$  to  $2\text{YCl}_3$ , this method has been carefully studied and we believe it to be the most satisfactory ratio yet proposed for the determination of the atomic weight of yttrium.

#### Experimental.

**Preparation of Material.**—The sources of material, the early treatment and the general methods of procedure have been presented in the preliminary paper<sup>1</sup> and will not be repeated here. An extensive study was made of three methods of purification and the results obtained will be discussed. In this study two methods were used to observe the effect of the treatment. The first was by means of the absorption spectra of the solutions, and the second was by watching the changes in the atomic weight of the material. For the latter work a portion of each fraction was carefully purified by dissolving the oxide in pure hydrochloric acid, reprecipitating twice with redistilled ammonia and twice with a hot solution of pure oxalic acid, each precipitate being thoroughly washed by several liters of boiling water. No effort was made in these trial determinations to remove the alkali metals, which probably accounts in part, at least, for the fact that the trial values run uniformly lower than the actual values.

In making the trial determinations of the atomic weights three methods were used. In the early part of the investigation the synthesis of the sulfate was tried but it was abandoned because of the difficulty of obtaining concordant results. A second method was then tried as follows: A weighed sample of the rare-earth oxide was dissolved in a known amount of 0.1 *N* sulfuric acid; there was added a quantity of a 5 *N* neutral solution of potassium oxalate slightly in excess of the amount needed to precipitate the rare earth present; and finally the excess of sulfuric acid was determined by titration with 0.1 *N* potassium hydroxide, using phenolphthalein as an indicator. This method is rapid and gives quite satisfactory results, although the presence of a rare-earth precipitate in the acid solution makes it difficult to obtain a sharp end point.

The third trial method used in observing the effect of the purification methods upon the yttria is as follows: Two samples of rare-earth oxalate

<sup>1</sup> THIS JOURNAL, 35, 365 (1913).

are weighed out, one in a small Erlenmeyer flask and the other in a platinum crucible. It is absolutely essential that these two samples be uniform in composition. The sample in the crucible is ignited to the oxide and the percentage of oxide in the oxalate determined. The sample in the flask is dissolved in a slight excess of dilute sulfuric acid and the amount of oxalic acid determined by titration with twentieth normal potassium permanganate. Then the percentage of oxalic acid in the oxalate is calculated and the atomic weight determined by the proportion

$$X + 24 : 108 = \text{percentage of oxide} : \text{percentage of oxalic acid}.$$

In order to make sure that the oxalate contained no water-soluble substances which would reduce the permanganate, samples were soaked for 50 hours in conductivity water, at the end of which time the water contained no reducing substance. While this method is somewhat more laborious than the preceding, it has been used more than either of the others for the reason that it gives more concordant results. A comparison of the three methods is shown in Table II, in which are recorded the atomic weights of certain fractions determined by more than one method.

TABLE II.  
Atomic weight determined by

Sample.	KMnO <sub>4</sub> titration.	KOH titration.	Sulfate.
1	89.30	90.12	.....
2	89.70	91.07	.....
3	88.88	89.70	.....
4	89.34	90.26	.....
5	93.76	.....	94.10
6	93.22	94.56	94.70
7	89.34	90.47	90.28

This table shows that the values obtained by the permanganate titration are somewhat lower than those obtained by the other methods and are probably no nearer the true value, but this method is preferred to the others because we have found it more reliable and hence more serviceable in determining the progress of the work. That the results from this method are too low is made evident by comparing the values obtained by its use with the atomic weights obtained by the use of the chloride method.

**The Chromate Method.**—An attempt was made to remove other less basic earths from yttrium by repeated treatment with the chromate method. The process was carried out exactly as described in the preliminary paper.<sup>1</sup> The fractions obtained in the previous chromate treatment were divided into five groups according to their atomic weight and each group was put through the chromate fractionation in a separate flask. The material used for this work contained considerable quantities of erbium and holmium and probably contained small amounts of other

<sup>1</sup> THIS JOURNAL, 35, 366 (1913).

rare earths, especially thulium, dysprosium and possibly terbium. Six fractions were precipitated with potassium chromate and the seventh and largest fraction was thrown down by potassium hydroxide. The results are shown in Table III.

TABLE III.

Flask.	Weight of oxide.	Av. at. wt.	Fractions obtained.	Atomic weight of last fraction.
I.....	160	92.9	7	90.3
II.....	160	92.4	7	89.2
III.....	153	90.8	7	89.1
IV.....	160	.... <sup>1</sup>	7	90.1
V.....	160	94.3	7	91.3

A second run was made in the same manner, using the last fractions from Flasks II and III in Flask I<sub>2</sub> and the last fractions from Flasks I and IV in Flask II<sub>2</sub>; Flask III<sub>2</sub> contained the seventh fraction from Flask V, together with a quantity of yttria of about the same atomic weight. The results are shown below:

TABLE IV.

Flask.	Weight of oxide.	At. wt. of orig. subs.	Fractions obtained.	At. wt. last fraction.
I <sub>2</sub> .....	160	89.15	8	89.35
II <sub>2</sub> .....	160	90.20	8	90.20
III <sub>2</sub> .....	160	91.35	8	90.90

These results show that the limit of efficiency of the chromate method had been reached since both Flasks I<sub>2</sub> and II<sub>2</sub> show the same atomic weight as the original material within the limits of experimental error of the sulfate method which was used to determine these values. Accordingly it was determined to take the material from the last fractions of the second run and try the efficiency of the fractional precipitation with dilute ammonia. The absorption spectra of the last fractions showed a slightly decreased intensity of the holmium lines, considerably less erbium and none of the other rare earths. This method apparently is not able to remove the last traces of either erbium or holmium.

**The Ammonia Method.**—Fractions 7 and 8 from both Flasks I<sub>2</sub> and II<sub>2</sub> and Fraction 8 from Flask III<sub>2</sub> were combined, giving 386 g. of yttrium oxalate, the average atomic weight of the yttrium being 90.31. This was ignited to the oxide, dissolved in HCl, evaporated to dryness and dissolved in about 5 liters of water. To this solution dilute ammonia was added, the mixture allowed to stand for 24 hours, the precipitate filtered out and the solution evaporated to its original volume, when the process was repeated. This material was subjected to 42 fractionations in this manner, the precipitates giving purified oxalates which averaged 3.1 g. in weight. The ammonia added was so dilute that there was no cloudiness when the solutions were first mixed, but on standing a faint precipi-

<sup>1</sup> Flask IV contained no material with higher atomic weight than 92, but the average atomic weight was not determined.

tate appeared. The early fractions were precipitated by two liters of ammonia which was 0.0125 *N*; then the strength was decreased to 0.01 *N* and the volume of precipitant increased to three liters. Fractions from this series are designated as H fractions.

In exactly the same way 37 fractions were obtained from a solution representing 246 g. of the purest oxalate obtained in the work described in the preliminary paper. When a saturated solution of the chloride of this material was examined with the spectroscope, no trace of holmium or dysprosium could be seen, but faint lines of erbium were visible. It was estimated to contain about 0.5 % of erbium salts. The fractions prepared from this material are designated as E fractions and the atomic weights obtained from various fractions of the two series are shown in Table V.

TABLE V.

	Atomic weights.	
	H series.	E series.
Fraction 1.....	94.7	91.2
Fraction 10.....	92.7	89.7
Fraction 15.....	91.8	89.8
Fraction 20.....	90.7	....
Fraction 25.....	90.2	88.7
Fraction 30.....	89.9	88.7
Fraction 35.....	89.9	88.7
Fraction 40.....	89.9	....

Fractional precipitation by dilute ammonia is slow, but is capable of removing the less basic earths from yttrium when they are present in considerable quantities. This method seems to be useless for removing the last traces of both erbium and holmium. That the E series gave material of lower atomic weight than the H series is undoubtedly due to the fact that the latter contained considerable holmium while the former was free from this element.

**Sodium Nitrite Method.**—An extensive study of the effects of fractional precipitation by sodium nitrite was made. This method suggested, by Holden and James,<sup>1</sup> consists in adding a strong solution of sodium nitrite to the nearly neutral solution of the rare-earth nitrates. We have found it expedient to modify in certain features the procedure recommended by Professor James and so our practice is given in full. A quantity of rare-earth oxide weighing from 80 to 110 g. was dissolved in pure nitric acid and the solution evaporated to dryness, care being taken not to overheat any portion. The residue was dissolved in water and made up to about 3 liters, then heated to boiling and a strong solution of sodium nitrite was added drop by drop from a separatory funnel while bumping was prevented by passing in a lively stream of steam. The boiling

<sup>1</sup> THIS JOURNAL, 36, 1419 (1914).

was continued from 30 to 90 minutes after the addition of the nitrite, then the solution allowed to stand, usually overnight, and the precipitate filtered out. The precipitate was dissolved in nitric acid and purified in the usual manner, while the process was repeated with the mother liquor. The nitrite used was of the C. P. grade, whose purity was proven by the U. S. P. test. The usual amount of nitrite added at a time was 35 g. dissolved in 70 cc. of water, but larger or smaller amounts were added, depending upon the number of fractions desired from any run. During the progress of the study it was discovered that if the rare-earth solutions were sufficiently dilute the nitrite could be added in the cold without the immediate formation of a precipitate, but upon boiling the mixture for a few minutes a cloudiness appeared and finally a precipitate settled out. This procedure was followed during the latter part of the study of this method since it seemed to give a slightly more rapid separation. We have also found it advisable to continue the fractional precipitation with sodium nitrite until all of the rare earth is thrown out of solution in place of precipitating the final fraction with oxalic acid.

The material first used in testing this method consisted of 80 g. of yttrium oxide which were obtained by adding oxalic acid to the mother liquor from the H ammonia series. The fractions are marked N fractions and the results are shown in Table VI.

TABLE VI.

Fraction.	Wt. of oxalate.	Color of oxalate.	At. wt.
N <sub>1</sub> .....	7.5	Slight pink	89.34
N <sub>2</sub> .....	16.5	Very slight pink	89.07
N <sub>3</sub> .....	30.4	Less than N <sub>2</sub>	88.78
N <sub>4</sub> .....	19.3	Almost white	88.95
N <sub>5</sub> .....	32.3	White	88.88
N <sub>6</sub> .....	26.4	White	88.85
N <sub>7</sub> .....	24.5	White	87.65
N <sub>8</sub> .....	1.7	White	87.56

The first fractions show an atomic weight lower than the original material, because the permanganate method was used to determine these atomic weights, while the values given in Table V were determined by titration with potassium hydroxide. It is to be noted that Fractions 3 to 6 yield atomic weights which are nearly or quite constant within the limit of error of the method used while Fractions 7 and 8 show a sharp and pronounced decrease. Fraction 8 was too small in quantity to permit an extended study of its composition but an effort was made to discover why Fraction 7 had so low a value. It was at first supposed that the purification of the sample used in determining the atomic weight had not been thoroughly done, so a fresh sample was put through the purification process. This portion gave an atomic weight of 87.77. Then it was thought that possibly these last fractions, being precipitated from

solutions which were becoming heavily loaded with sodium salts, had dragged down enough sodium to account for the low value. So another sample was very thoroughly purified including two precipitations with ammonium sebacate in order to free the yttria from sodium compounds. The material purified in this way gave yttrium an atomic weight of 87.75. Finally the material was tested for scandium by adding a saturated solution of  $K_2SO_4$  to a nearly saturated solution of the rare-earth chloride but no trace of scandium could be detected. Efforts to detect a similar drop in the end fractions of other runs have not been wholly successful, although attention should also be directed to the fact that a similar drop in atomic weight in the last fraction is to be observed in many of the tables given by Holden and James.<sup>1</sup> We are not now prepared to offer an explanation of this peculiar phenomenon.

In order to test further the efficiency of the nitrite method of fractional precipitation, Fractions 3, 4, 5 and 6 of the N series were combined, giving 106.2 g. of material with an average atomic weight of 88.87. This was fractionated again, six fractions being obtained and designated as O fractions, which are described in Table VII.

TABLE VII.

Fraction.	Wt. of oxalate.	Color of oxalate.	Atomic weight.
O <sub>1</sub> .....	10.1	•Very slightly yellow	89.18
O <sub>2</sub> .....	18.2	Faint pink tint	89.42
O <sub>3</sub> .....	14.5	White	88.69
O <sub>4</sub> .....	23.7	White	88.46
O <sub>5</sub> .....	17.8	White	88.42
O <sub>6</sub> .....	4.6	White	88.48

Solutions of Fractions 4, 5 and 6 showed no trace of absorption lines, so it was concluded that both erbium and holmium had been eliminated.

A quantity of yttria equivalent to 37 g. was collected from the last fractions of the E ammonia series (Table V) and subjected to the nitrite fractional precipitation. The original solution showed very slight traces of erbium but there seemed to be no other rare-earth admixture. The results are shown in Table VIII.

TABLE VIII.

Fraction.	Wt. of oxalate.	Color of oxalate.	Atomic weight.
R <sub>1</sub> .....	16.3	White	88.58
R <sub>2</sub> .....	36.3	White	88.50
R <sub>3</sub> .....	9.0	White	88.40
R <sub>4</sub> .....	6.8	White	88.45
R <sub>5</sub> .....	1.4	White	88.42

Solutions from the last three fractions showed no visible absorption lines. The oxide obtained from the later fractions is pure white except for a very faint brownish tint which appears wherever the oxide is heated in contact with platinum.

<sup>1</sup> THIS JOURNAL, 36, 1418-23 (1914).

To test the efficiency of the nitrite fractionation when less pure material is used, 639 g. of yttria from a separate series of bromate fractionations<sup>1</sup> and 583 g. of yttria from the early fractions of the chromate series (Tables III and IV) were converted into the nitrate, which was dissolved in 30 liters of water and neutralized with a dilute solution of sodium hydroxide. This solution contained in a 65 liter evaporating dish was heated over a steam bath and live steam was introduced directly into the solution by means of a perforated block tin coil connected with high pressure steam. A porcelain baffle plate prevented splashing during the heating. Six fractions averaging 364 g. in weight were obtained, the color of the fractions changing gradually from a distinct pink in the first to pure white in the sixth. The original material showed an atomic weight of 91.85 and the lines of both erbium and holmium were distinctly visible. The atomic weight of the yttrium in the sixth fraction was 89.73 and this material, equivalent to 135 g. of the oxide, was again fractionated by the nitrite method, thirteen fractions being obtained. A faint pink color was apparent in the first three fractions, but the others were pure white. The atomic weight of the yttrium in the fourth fraction was 89.75, this value decreasing gradually to 88.73 in the thirteenth fraction. The lines of both holmium and erbium were still faintly visible in these later fractions, but we are convinced not only that the nitrite method of fractionation produces pure yttria, but also that it serves as a rapid and convenient method of removing both erbium and holmium whether they are present in large or small quantities.

#### The Hydrated Yttrium Salts.

With the hope of finding the hydrated salts of yttrium sufficiently stable under some conditions to be used in atomic weight determinations, samples of  $Y_2(SO_4)_3 \cdot 8H_2O$  and  $YCl_3 \cdot 6H_2O$  were prepared. For the preparation of the former, 22.4 g. of oxalate from H ammonia fractions 17, 22, 24, 27 and 28 (Table V) were ignited to the oxide, dissolved in HCl, a small excess of  $H_2SO_4$  added, the solution evaporated to dryness, and the residue heated in an electric furnace at  $525^\circ$  for four hours. The crystals were dissolved in water by the aid of an agitating machine and the solution evaporated to crystallization. The crystals were thoroughly drained from the mother liquor in a powerful centrifuge and the crystallization repeated. Finally the crystals were allowed to dry in air for 24 hours. These crystals were then divided into five parts and each part was placed in a porcelain crucible. One of the parts was heated until it was certain that a portion of the water of hydration had been expelled. Each of the other crucibles was placed in a weighing bottle and the bottle with cap removed was placed in a desiccator. One desiccator had an opening to the air but contained no desiccating agent, the second contained sulfuric

<sup>1</sup> The bromate fractionation was performed by Dr. E. W. Engle.

acid, the third calcium chloride, and the fourth contained the partially dehydrated sulfate. In this manner it was hoped to discover the conditions under which the hydrates would be stable. At intervals the weighing bottles were closed and the weight determined as shown in Table IX.

TABLE IX.

Date.	In air.	Over $\text{H}_2\text{SO}_4$ .	Over $\text{CaCl}_2$ .	Over partly dehydrated sulfate.
Jan. 3	....	18.3387	17.2310	16.9220
Jan. 6	15.5649	18.3376	17.2293	16.9205
Jan. 8	15.5649	18.3381	17.2300	16.9212
Jan. 12	15.5641	18.3371	17.2290	16.9201
Jan. 14	15.5642	18.3373	17.2291	16.9203
Jan. 19	....	18.3367	17.2284	16.9196
Jan. 22	15.5637	18.3367	17.2285	16.9197
Jan. 24	15.56401	18.33717	17.22882	16.92013
Feb. 4	15.56394	18.33719	17.22874	16.91979
Feb. 7	15.56388	18.33701	17.22807	16.91961
Mar. 7	15.56373	18.33667	17.22784	16.91948
Mar. 24	15.56366	18.33672	17.22786	16.91944
Apr. 5	15.56352	18.33648	17.22771	16.91953

In a similar manner 17.2 g. of yttrium oxalate from ammonia fractions E 12, 13, 18 and 21 (Table V) were converted into  $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$  and their stability tested in air, over sulfuric acid, over calcium chloride, and over the partially dehydrated yttrium chloride. The weights are shown in Table X.

TABLE X.

Date.	In air.	Over $\text{H}_2\text{SO}_4$ .	Over $\text{CaCl}_2$ .	Over partly dehydrated chloride.
Feb. 4	13.4313	14.8756	13.8957	13.5841
Feb. 5	13.4321	14.8761	13.8967	13.5849
Feb. 6	13.4317	14.8761	13.8963	13.5846
Feb. 7	13.43159	14.87592	13.89627	13.58393
Feb. 16	13.43138	14.87568	13.89611	13.58378
Feb. 25	13.43132	14.87574	13.89618	13.58370
Mar. 7	13.43145	14.87563	13.89618	13.58368
Mar. 24	13.43130	14.87563	13.89614	13.58369
Apr. 5	13.43125	14.87546	13.89608	13.58366

The hydrates did not seem to be stable under any of these conditions, consequently this effort was abandoned.

### The Atomic Weight.

**Preparation of Reagents.**—The reagents used in the final treatment of the yttria preparatory to determining the atomic weight were all carefully purified in this laboratory. Hydrochloric acid was distilled in glass; nitric acid was distilled in quartz and kept in a quartz bottle; ammonia was freshly distilled as needed from a quartz flask into conductivity water contained in quartz. Ammonium sebacate was prepared by suspending the purest sebacic acid in conductivity water into which



ammonia was distilled until the acid had dissolved; then the sebacate was recrystallized twice, the crystals being thoroughly freed from the mother liquor with the centrifuge. Oxalic acid was purified in the following manner: C. P. crystals were dissolved in water containing a small amount of nitric acid; the solution was evaporated to crystallization on the steam bath and then stirred constantly until cold. The fine crystals were freed from the mother liquor in a large centrifuge and recrystallized twice from dilute nitric acid solution, and twice from pure water. The oxalic acid prepared in this manner left no weighable residue on ignition.

**The Yttrium Material.**—The fractions selected for use in the determination of the atomic weight were O fractions 4, 5 and 6 (Table VII) and R fractions 3, 4 and 5 (Table VIII). The three O fractions were mixed, ignited to the oxide, then dissolved in redistilled hydrochloric acid and reprecipitated twice with freshly distilled ammonia. The precipitates were filtered out on a Büchner funnel and washed with several liters of boiling water, care being taken to keep the precipitate hot and flocculent. Then the yttrium material was precipitated twice from an acid solution with pure oxalic acid, twice with ammonium sebacate, and finally with oxalic acid. The yttria was converted into the chloride in a platinum dish, the solution evaporated and left in a vacuum desiccator to crystallize. Only the first crop of crystals were used in the atomic weight work.

The R fractions were purified in a similar manner, except that they were not mixed and the transformation to the chloride was omitted.

The purification of the yttrium material and the preparation of the reagents were made in a room in which no other work was permitted. Great care was exercised to keep the atmosphere of the room free from laboratory gases and the material free from dust.

**The Determinations.**—The apparatus used was similar in principle to that previously described.<sup>1</sup> The drying trains for gases were modified so that all reagents were applied in towers filled with glass beads, making a more compact apparatus. The quartz reaction flasks<sup>2</sup> used were somewhat smaller and lighter than those previously employed. When in use the flask was surrounded by an asbestos oven, which served partly to protect it from the laboratory atmosphere. Within the oven was placed an electric furnace which was provided with a double winding of nichrome wire in such a manner that by the use of external resistance any temperature between that of the room and 1000° or more could be maintained. In order to hasten as much as possible the process of dehydration the gases entering the reaction flask were preheated by passing through a glass coil enclosed within the oven.

<sup>1</sup> THIS JOURNAL, 35, 373 (1913).

<sup>2</sup> *Ibid.*, 35, 373 (1913).

The manipulation was exactly the same as that described in the preliminary paper, except that after the oxide was weighed in the flask, it was dissolved in redistilled hydrochloric acid before the flask was attached to the drying train. This procedure shortened the time during which the flask was exposed to the laboratory atmosphere. Weights were made by substitution, using as tare a quartz flask differing in weight from the reaction flask by only a few milligrams. The weights were recently standardized and in all but the first two determinations the weighings were made in a special insulated balance room. The values obtained are shown in Table XI, correction having been made for air displacement.

TABLE XI.

No.	Material.	Weight of oxide.	Weight of chloride.	Atomic weight.
1.....	O <sub>4</sub> s	0.56492	0.97718	88.89
2.....	O <sub>4</sub> s	0.51059	0.88348	88.80
3.....	R <sub>5</sub>	0.64232	1.11092	88.92
5.....	R <sub>4</sub>	0.82157	1.42087	88.93
6.....	R <sub>3</sub>	0.68246	1.17975	89.06
7.....	O <sub>4</sub> s	0.54164	0.93688	88.89

The fourth determination was lost. No reason is known for the low value in the second except that some difficulty was experienced in getting complete dehydration in this case, due probably to the fact that an attempt was made to shorten the process by dehydrating the crystals formed from the strongly acid solution instead of dissolving them in water and dehydrating the crystals formed from a nearly neutral solution. The high value obtained from R<sub>3</sub> may be due to the fact that this fraction was not quite as pure as the others. The R fractions give slightly higher values than the O fractions, but the rather close check obtained from these different fractions would indicate that the yttria is of a high degree of purity. These results have an average of 88.91, which is somewhat higher than the accepted value (88.7).

The advantages claimed for this method are as follows: (1) the use of a ratio which is independent of the sulfate; (2) simplicity in manipulation; and (3) the fact that there are no transfers during the process.

There are several sources of error which have been carefully guarded against. The length of time which is needed to complete a determination makes it necessary for the reaction flask to be exposed to the laboratory atmosphere for several days, during which condensations might easily take place upon the surface. In order to prevent this the flask was tightly inclosed in the drying oven, the lead tubes were kept covered, and the dehydration was finished within as short a time as possible. After the chloride had been fused the flasks were carefully wiped with a clean linen cloth. Care was then exercised to remove any electrification which might have been caused by the friction.

The volatility of yttrium chloride was a matter of some concern, and for this reason the fusion of the chloride was always made with the direct flame. In this way the temperature was raised quickly to the fusion point and as quickly lowered again. The exit tubes were always examined closely for evidences of a deposit and in no case was there the slightest indication of a deposit on the tube B<sup>1</sup> or the upper part of the side neck near D'. There was a slight deposit on the lower portions of this side neck, but since the tube B was included in the weighed portion of the flask it is improbable that any material was lost through volatilization.

In order to learn if fused yttrium chloride adsorbs HCl as it cools, a simple modification of the usual procedure was undertaken. After the chloride was fused in an atmosphere of hydrogen chloride, it was customary to allow it to cool to about 350° and then replace the HCl with nitrogen as the cooling continued. In the last determination (No. 7) the fused chloride was allowed to cool to room temperature in the atmosphere of HCl. In this way it was expected that the acidity of the chloride would be increased if HCl had been adsorbed. There was no increase in acidity, hence it was concluded that there was little or no adsorption.

#### Summary.

1. Determinations of the atomic weight of yttrium by the synthesis of the sulfate are not reliable since the value may be made to vary widely by changing the length of time and the temperature of ignition.

2. In preparing pure yttria three methods of fractional precipitation were applied to partially purified material.

(a) Fractional precipitation with potassium chromate is effective for removing considerable quantities of other rare earths from yttrium but will not remove all the erbium or holmium.

(b) Fractional precipitation with dilute ammonium hydroxide is tedious and does not produce pure yttria.

(c) Fractionation with sodium nitrite is both a rapid and effective means of freeing yttrium material from admixtures of erbium and holmium.

3. Solutions of materials prepared by the use of all three of these methods gave no visible absorption lines and seemed to be pure yttria.

4. The hydrates  $Y_2(SO_4)_3 \cdot 8H_2O$  and  $YCl_3 \cdot 6H_2O$  are found to be too variable to permit of their use in atomic weight work.

5. The atomic weight of yttrium was determined by the ratio  $Y_2O_3 : 2YCl_3$  using material from six different fractions. The average of the values obtained is 88.9.

The work is to be continued with two points in view: (1) to study further the purity of the yttria, and (2) to attempt to apply other ratios to the determination of the atomic weight of yttrium.

URBANA, ILL.

<sup>1</sup> See figure, *THIS JOURNAL*, 35, 373 (1913).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

## THE FREE ENERGY OF BROMINE COMPOUNDS.

BY GILBERT N. LEWIS AND MERLE RANDALL.

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Taking as the standard state of bromine the one which is stable at 25° and a pressure of one atmosphere, namely liquid bromine, we are in a position to calculate the free energy of the various known forms of elementary bromine, of bromide and polybromide ions, and of all the known compounds of bromine with oxygen and hydrogen.

### Elementary Bromine.

$2\text{Br}(l) = \text{Br}_2(g)$ .—The vapor pressure of liquid bromine has been determined by Roozeboom<sup>1</sup> and by Ramsay and Young.<sup>2</sup> Both sets of measurements show excellent self-consistency when tested by plotting  $\log p$  against  $1/T$ . In both cases a few scattering points are obviously in error, but the remaining points give for each set a straight line, and these two straight lines are not only near to one another but are parallel, that is, they have the same slope. From this slope we may determine directly the heat of vaporization at the average temperature (32°) of the points which were plotted. We thus find  $\Delta H_{305} = 7530$ . The heat capacity of liquid bromine has not been accurately determined but we may take as an approximate value for this reaction  $\Delta F = -9.6$ . Since we have adopted permanently for  $\text{Br}_2(g)$  the value<sup>3</sup>  $C_p = 6.5 + 0.004T$ , this means that we are taking for  $\text{Br}(l)$ ,  $C_p = 8.05 + 0.002T$ , an equation which is purely formal, introduced for convenience, and only has experimental significance inasmuch as it gives the approximate value of the specific heat of liquid bromine at room temperature. Having once assumed this equation we must of course apply it consistently in our future equations. We therefore write  $\Delta H = 10450 - 9.6 T$ , which agrees almost precisely with the heat of vaporization determined by Berthelot at 60° and is a trifle higher than the value obtained by Thomsen. The final free energy equation is

$$\Delta F^\circ = 10450 + 9.6T \ln T - 87.21T, \quad (1)$$

where the value of  $I = -87.21$  is obtained from the following determination of  $\Delta F^\circ_{298}$ . The vapor pressure of bromine at 25° is 208 mm. of mercury if we use the data of Roozeboom, and 213 mm. if we use the data of Ramsay and Young. The latter measurements are in somewhat better agreement with the determinations of the boiling point of bromine, and we shall therefore accept Ramsay and Young's value. Hence,

$$\Delta F^\circ_{298} = 755 \text{ cal.} \quad (2)$$

<sup>1</sup> Roozeboom, *Rec trav. chim.*, 3, 73 (1884).

<sup>2</sup> Ramsay and Young, *J. Chem. Soc.*, 49, 453 (1886).

<sup>3</sup> Lewis and Randall, *THIS JOURNAL*, 34, 1128 (1912).

We may use Equation 1 to find the boiling point of bromine by writing  $\Delta F^\circ = 0$  and solving for  $T$ . This gives  $58.7^\circ$ . Such a calculation from an equation like (1) is very instructive, since it shows at once the necessity of the very highest numerical accuracy, notwithstanding the fact that such a coefficient as that of  $T \ln T$  is uncertain, and that the original choice of this constant, rather than some neighboring one, is not very important. It will of course be obvious that such an equation will not be valid over a very wide temperature interval, and if it is so used it will be in a purely formal manner. It must also be noted that we have throughout assumed bromine vapor to be a perfect gas. If reliable data concerning the density and compressibility of the vapor were available we should take as the normal state of  $\text{Br}_2(\text{g})$  not the gas at one atmosphere but in the condition where its activity is  $x$  times as great as at  $1/x$  atmos., where  $x$  is a large number.

$\text{Br}(\text{l}) = \text{Br}(\text{s})$ .—The heat of fusion of bromine was found by Regnault to be 1290 cal. per gram atom. The heat capacity of solid bromine has not been much studied, but judging from the measurements of Koref<sup>1</sup> at low temperatures it is not far from that of liquid bromine at ordinary temperatures. We may write, therefore,  $\Delta F^\circ = 0$  and  $\Delta H_0 = -1290$ . Taking the freezing point as  $-7.3^\circ$  where  $\Delta F^\circ = 0$ , we find

$$\Delta F^\circ = -1290 + 4.86T; \Delta F_{298}^\circ = 157. \quad (3)$$

Without a direct determination of either melting point or heat of fusion we could make this same calculation from the experiments of Ramsay and Young and those of Cuthbertson<sup>2</sup> upon the vapor pressure of solid bromine. We have plotted their data in the usual way, namely,  $\log p$  against  $1/T$ . From the slope of the curve, which gives the heat of sublimation, and from the heat of vaporization of the liquid which we have already discussed, we find a value for the heat of fusion of 1245 cal., which, within the limits of error of the vapor-pressure measurements, coincides with the value of Regnault. Likewise from the vapor-pressure measurements we could calculate directly the value of  $\Delta F_{298}^\circ$ , and here too the calculation, although subject to large errors, agrees with the value which we have given. Similar calculations, based upon more accurate data, we have already made in discussing the various forms of elementary sulfur.<sup>3</sup>

$\text{Br}_2(\text{g}) = \text{Br}_2(\text{in CCl}_4, N = 1)$ .—Before proceeding to determine the free energy of aqueous bromine, partly as a step in this process, but also on account of the frequent use of carbon tetrachloride as a solvent in distribution experiments, and in general where it is necessary to maintain a phase in which the activity of the solute is kept at a known constant value, it will be desirable to calculate the free energy of bromine dissolved

<sup>1</sup> Koref, *Ann. Physik*, [4] 36, 49 (1911).

<sup>2</sup> Cuthbertson, *Proc. Roy. Soc., (A)* 85, 306 (1911).

<sup>3</sup> Lewis and Randall, *THIS JOURNAL*, 36, 2468 (1914).

$\text{CCl}_4$ . Since carbon tetrachloride as a nonpolar substance has essentially the characteristics of a normal liquid, it will be preferable to use a convention for the standard condition in this solvent differing from the one which we have employed in the case of water. We shall therefore use not the concentration of the solute but its mol fraction,  $N$ , and we shall take as a standard or normal condition<sup>1</sup> the one in which the activity (or vapor pressure) is  $1/N$  times as great as that in a dilute solution in which the mol fraction of the solute is  $N$ . Mr. Storch, in this laboratory, has made a number of determinations, which will shortly be published, of the vapor pressure of bromine from dilute solutions in  $\text{CCl}_4$ . He finds at  $25^\circ$ ,  $p = 0.539 N$ , where  $p$  is the partial vapor pressure of  $\text{Br}_2$  in atmospheres and  $N$  is its mol fraction. The measurements extend from  $N = 0$  to  $N = 0.025$ . It is evident that the solution of  $\text{Br}_2$  in  $\text{CCl}_4$  does not obey Raoult's law over the whole range of concentrations, for the equation would lead when  $N = 1$  to a vapor pressure nearly twice that of pure liquid bromine. Our free energy equation in this case is simply

$$\Delta F^\circ_{298} = -RT \ln (N/p) = -366. \quad (4)$$

$2\text{Br}(g) = \text{Br}_2$  (in  $\text{CCl}_4$ ,  $N = 1$ ).—Adding Equations 2 and 4 gives

$$\Delta F^\circ_{298} = 389 \text{ cal.} \quad (5)$$

$\text{Br}_2$  (in  $\text{CCl}_4$ ;  $N = 1$ ) =  $\text{Br}_2(\text{aq})$ .—In discussing the distribution of bromine between water and carbon tetrachloride we shall use the mol fraction of the bromine to express the composition of the  $\text{CCl}_4$  phase and, as usual, mols  $\text{Br}_2$  to 1000 g. of water to express that of the aqueous phase. The well-known experiments of Jakowkin,<sup>2</sup> on the distribution coefficient in this system, we have reviewed in detail and we arrive at conclusions which differ somewhat from those which have usually been drawn from these measurements. His experiments in dilute solutions are vitiated by the fact that the bromine hydrolyzes in the aqueous phase to the extent of 10% or more<sup>3</sup> and his figures are for the total bromine and not for that which occurs simply as  $\text{Br}_2$ . Mr. Storch in hitherto unpublished work, to which we have referred, has determined the partition of bromine between  $\text{CCl}_4$  and water containing  $\text{HCl}$  at  $0.001M$ . It was assumed that water containing this small amount of hydrochloric acid, would prevent the hydrolysis of the bromine, but would not affect materially the activity of the dissolved  $\text{Br}_2$ . In order to test this assumption similar partition experiments were made between  $\text{CCl}_4$  and water containing

<sup>1</sup> The advantage of this choice is obvious in the case of two liquids which like benzene and toluene in all mixtures form perfect solutions (see Lewis, *THIS JOURNAL*, 30, 668 (1908)). Here it is evident that  $F^\circ$  is the same for  $\text{C}_6\text{H}_6$  ( $l$ ) and  $\text{C}_6\text{H}_6$  (in toluene).

<sup>2</sup> Jakowkin, *Z. physik. Chem.*, 18, 583 (1895).

<sup>3</sup> Bray and Connolly, *THIS JOURNAL*, 33, 1485 (1911).

an equivalent amount of sulfuric acid. He found for  $m/N$ , 0.3705 with HCl and 0.3710 with  $H_2SO_4$ , where  $N$  is the mol fraction of  $Br_2$  in the  $CCl_4$  and  $m$  the number of mols per 1000 g.  $H_2O$ . We shall write  $m/N = 0.371$ . In these measurements  $N$  was equal to 0.01373. When we consider Jakowkin's experiments at the higher concentrations, where hydrolysis plays no important role, we find that this partition coefficient, owing to the high concentrations, varies more than the ratio which we use involving the mol fraction instead of the concentration. Without repeating the rather laborious calculations which we have made in reducing his measurements to our units (assuming that  $Br(l)$  and  $CCl_4$  mix without change of volume) we may state merely that the value of  $m/N$  varies regularly from 0.35 at  $N = 0.14$  to values in dilute solutions which agree closely with the one obtained by Storch, 0.371. Taking this value as the partition ratio in dilute solution we find for this reaction

$$\Delta F^\circ_{298} = -R'T \ln(m/N) = 588. \quad (6)$$

$2Br(l) = Br_2(aq)$ .—Adding Equations 5 and 6 we find

$$\Delta F^\circ_{298} = 977. \quad (7)$$

Such an equation as (7) is of course applicable only to solutions which are so dilute that the activity of the solute is proportional to the concentration. It is interesting to see the magnitude of the deviation from such proportionality in the case of a saturated aqueous solution of bromine by comparing the measured solubility of bromine with that obtained from Equation 7. Bray and Connolly<sup>1</sup> found for the saturated solution of bromine at 25°,  $m = 0.2068$ , whereas from Equation 7, writing 977 =  $-R'T \ln m$ ;  $m = 0.1923$ , a difference of 7.5%.

$Br_2(g) = 2Br(g)$ .—The dissociation of bromine vapor into the monatomic gas has been studied by Perman and Atkinson<sup>2</sup> who measured the density of bromine vapor between 650° and 1050°. Their method of calculation is not easy to follow, but if we divide what they call vapor density by 80.3, which seems to be the best value of this quantity at the lowest temperature (where we may assume that no dissociation occurs) we should get the ratio between the actual density and the density calculated on the assumption of no dissociation. The equilibrium constants,  $K_p$ , calculated from these ratios, are given in the second row of Table I, the absolute temperature being given in the first row.

TABLE I.

T.....	1073	1123	1173	1223	1273	1323
$K_p$ .....	0.000179	0.000403	0.00140	0.00328	0.0077	0.0182

Now if we plot  $\log K_p$  against  $1/T$  we find that at the four highest temperatures, which are the only ones at which the dissociation is considera-

<sup>1</sup> Bray and Connolly, *THIS JOURNAL*, 33, 1485 (1911).

<sup>2</sup> Perman and Atkinson, *Z. physik. Chem.*, 33, 215, 577 (1900).

ble, the points lie on a straight line and the slope of this line multiplied by 4.579 gives at the average temperature of the measurements  $\Delta H_{1250} = 53700$ . Assuming that Br has the same heat capacity as other monatomic gases,  $\Delta \Gamma = 3.5 - 0.004T$ , whence  $\Delta H_0 = 52400$ , and

$$\Delta F^\circ = 52400 - 3.5T \ln T + 0.002T^2 - 9.07T \quad (8)$$

where the value of  $I = -9.07$  was obtained from  $\log K_{1250} = -2.27$  as read from the plot. Since the calculation of  $\Delta H$  from the density measurements is greatly affected by small errors, the value of  $\Delta F^\circ_{298}$  may easily be in error by several thousand calories. We have

$$\Delta F^\circ_{298} = 43900. \quad (9)$$

**Br(l) = Br(g).**—Combining Equations 1 and 2, respectively, with 8 and 9,  $\Delta F^\circ = 31425 + 3.05T \ln T + 0.001T^2 - 48.14T$ ;

$$\Delta F^\circ_{298} = 22328. \quad (10)$$

### Hydrobromic Acid; Bromide Ion; Tribromide Ion; Pentabromide Ion.

$\frac{1}{2}H_2 + \frac{1}{2}Br_2(g) = HBr(g)$ .—The dissociation of gaseous hydrogen bromide has been investigated by von Falckenstein<sup>1</sup> at the temperatures 1024°, 1108° and 1222°. His measurements lead directly to the corresponding three values of  $\log K_p$ , 2.60, 2.44 and 2.27.

In order to calculate from these measurements the free energy of this reaction at other temperatures we must know the thermal quantities involved. The heat capacities of the three gases are given in our former paper<sup>2</sup> and thence we find  $\Delta \Gamma = -0.00145T$ . The heat of the reaction at room temperatures calculated from the measurements of Thomsen is 11900, and from those of Berthelot 12300, average 12100, and  $\Delta H_0 = -12000$ . The complete free energy equation is therefore

$$\Delta F^\circ = -12000 + 0.000725T^2 - 3.5T, \quad (11)$$

where the value of  $I$ ,  $-3.5$ , is the mean of the values obtained at von Falckenstein's three temperatures, namely,  $-3.57$ ,  $-3.46$ , and  $-3.43$ . Hence

$$\frac{1}{2}H_2 + \frac{1}{2}Br_2(g) = HBr(g); \Delta F^\circ_{298} = -12970. \quad (12)$$

While the extrapolation to 25° from von Falckenstein's experiments is made over a wide temperature range, the probable errors in the specific heats and in the heat of reaction are not sufficient to produce an uncertainty of more than 100 to 150 cal. in the value of  $\Delta F^\circ_{298}$ . This calculation therefore is probably at least as reliable as one which we shall now make and which is based upon the measurements by Bodenstein and Geiger<sup>3</sup> of the e. m. f. of the hydrogen, bromine, hydrobromic acid cell. They used two half cells both containing the same concentrated aqueous

<sup>1</sup> von Falckenstein, *Z. physik. Chem.*, **68**, 270 (1909).

<sup>2</sup> Lewis and Randall, *THIS JOURNAL*, **34**, 1128 (1912).

<sup>3</sup> Bodenstein and Geiger, *Z. physik. Chem.*, **49**, 70 (1904).



hydrobromic acid. In one was a hydrogen electrode, in the other a bromine electrode, enough bromine being added to the hydrobromic acid so that the vapor pressures of the bromine and hydrobromic acid could be simultaneously determined. Knowing then the vapor pressure of  $\text{Br}_2$ ,  $\text{HBr}$  and  $\text{H}_2$ , the electromotive force should be represented by the equation

$$E = E^\circ - \frac{RT}{F} \ln \frac{[\text{HBr}]}{[\text{H}_2]^{1/2} [\text{Br}_2]^{1/2}}.$$

The three cells in which Bodenstein and Geiger measured the electromotive forces and vapor pressures give for  $E^\circ$  the values 0.557, 0.558 and 0.549 v. at  $30^\circ$ . The differences between these values of  $E^\circ$  may be partly due to experimental error, but they must in part be due to the error in assuming the hydrobromic acid to be the same in the two halves of the cell, even though enough bromine is added on one side to change appreciably the vapor pressure of  $\text{HBr}$ , as shown by the authors themselves. The mean of their values gives  $\Delta F^\circ_{303} = -12760$ , or making the slight correction to  $25^\circ \text{ C.}$ ,  $\Delta F^\circ_{298} = -12740$ . Their value therefore agrees as well as could be expected with the one which we have given above. We shall accept the values obtained in Equations 11 and 12.

Before leaving Equation 11 it may be worth while to make a comment, which, though obvious when stated, has not to our knowledge previously been made. Ordinarily it has been assumed that in a reaction like the dissociation of  $\text{HBr}$  the degree of dissociation would, except for a possible change in the sign of the heat of reaction, increase with the temperature, and that at very high temperatures the dissociation would be complete. This is by no means the case. We have hitherto considered three reactions, namely, the dissociation of  $\text{NO}$ , of  $\text{HI}$  and of  $\text{HBr}$ , in which neither the number of molecules nor the number of atoms within a molecule changes. In such cases, as was first pointed out by Haber, not only is  $\Delta F$  small and the heat of reaction nearly constant, but the value of  $I$  is small and the free energy equation approximates closely to the simplest form  $\Delta F^\circ = \Delta H_0$ . In such a case it is evident, since  $-RT \ln K = \Delta F^\circ = \text{constant}$ , that as the temperature is indefinitely increased  $\ln K$  must approach zero, and therefore  $K$  must approach unity. In other words, the degree of dissociation will approach 50% and not 100% as the temperature is increased. In the actual cases which we have considered there are additional small terms in the free energy equation, but nevertheless it is evident that in any temperature range in which Equation 11 is approximately valid the degree of dissociation of  $\text{HBr}$  cannot exceed 50%, except of course insofar as other reactions enter, such as the dissociation of  $\text{H}_2$  and  $\text{Br}_2$  into their monoatomic forms.

$\frac{1}{2}\text{H}_2 + \text{Br}(l) = \text{HBr}(g)$ .—Combining Equations 1 and 2, respectively, with Equations 11 and 12, we find

$$\Delta F^{\circ} = -6775 + 4.8T \ln T + 0.000725T^2 - 47.10T; \Delta F^{\circ}_{298} = -12592. \quad (13)$$

$\text{Br}(l) + \ominus = \text{Br}^-$ .—The free energy of formation and of dilution of aqueous hydrobromic acid have been exhaustively investigated by Lewis and Storch in the paper to which we have already referred and which will shortly be published. As the final result of this investigation, against the standard hydrogen electrode, at  $25^{\circ}$ , the potential of liquid bromine in the presence of bromide ion at (hypothetical) molal concentration is  $-1.0659$  v., a value which is accurate to within a few tenths of a millivolt. Hence for the above reaction

$$\Delta F^{\circ}_{298} = -nE^{\circ}F' = E^{\circ}F'; \text{ or } \Delta F^{\circ}_{298} = -24594. \quad (14)$$

$\text{Br}^- + \text{Br}_2(\text{aq}) = \text{Br}_3^-$ .—The equilibrium in the formation of tribromide was studied by Jakowkin<sup>1</sup> who determined the partition of bromine between carbon tetrachloride and aqueous solutions of KBr at  $25^{\circ}$ . Assuming that  $\text{KBr}_3$  and KBr are in dilute solution ionized to the same extent at the same concentration, the ratio of  $\text{KBr}_3$  to KBr should be approximately constant. In fact a complete recalculation of Jakowkin's data gives a much better constant than he himself obtained. In this calculation we have used the partition coefficient given above, after recalculating his concentrations in  $\text{CCl}_4$  to mol fractions. The results of Jakowkin, as recalculated, are given in Table II. We have used only his measurements with dilute KBr and dilute  $\text{Br}_2$ . The first column gives the concentration of  $\text{Br}_2$  as such in the aqueous phase, the second the concentration of KBr used, and the third column the values of the constant  $K = (\text{Br}_3^-)/[(\text{Br}^-)(\text{Br}_2)]$ .

TABLE II.

$\text{Br}_2$ .	KBr.	K.
0.00198	0.0625	16.50
0.00377	0.0625	16.15
0.00710	0.0625	16.07
0.00986	0.0625	16.04
0.00145	0.1250	16.32
0.00345	0.1250	16.35
0.00610	0.1250	16.20
0.00880	0.1250	16.05

Dr. Linhart in this laboratory has made calculations based upon Worley's measurements<sup>2</sup> in more concentrated solutions and has shown that, when due allowance is made for the formation of pentabromide, Worley's measurements lead to the same constant as Jakowkin's. Moreover, Jakowkin's measurements are corroborated by the similar investigation of Storch with solutions of HBr. Taking  $K = 16.2$  we find

$$\Delta F^{\circ}_{298} = -1650. \quad (15)$$

<sup>1</sup> Jakowkin, *Z. physik. Chem.*, 20, 19 (1896).

<sup>2</sup> Worley, *J. Chem. Soc.*, 87, 1118 (1905).

$3\text{Br}(l) + \ominus = \text{Br}_3^-$ .—Adding Equations 7, 14 and 15, we find

$$\Delta F_{298}^\circ = -25267. \quad (16)$$

$\text{Br}_3^- + \text{Br}_2(\text{aq}) = \text{Br}_5^-$ .—There can hardly be any doubt that not only tribromide but higher polybromides exist in solution. Nevertheless, since a substance like  $\text{KBr}_5$  is formed in appreciable amounts only when the concentration of bromine is high, and therefore the laws of the dilute solution are not necessarily valid, the calculation of such a constant as  $(\text{Br}_5^-)/(\text{Br}_2)(\text{Br}_3^-)$  is attended with considerable uncertainty. The calculations made by Linhart from the experiments of Worley show very fair constancy in  $K$ , which he takes as 1.2, whence we may obtain as an approximate value

$$\Delta F_{298}^\circ = -110. \quad (17)$$

$5\text{Br}(l) + \ominus = \text{Br}_5^-$ .—Adding Equations 7, 16 and 17,

$$\Delta F_{298}^\circ = -24400. \quad (18)$$

$\text{Br}_2(\text{aq}) + \text{H}_2\text{O}(l) = \text{H}^+ + \text{Br}^- + \text{HBrO}(\text{aq})$ .—From careful measurements of the conductivity, Bray and Connolly<sup>1</sup> have determined the degree of hydrolysis of bromine solutions and found

$$K_{298} = (\text{H}^+)(\text{Br}^-)(\text{HBrO})/(\text{Br}_2) = 5.2 \times 10^{-9}.$$

Hence

$$\Delta F_{298}^\circ = 11310. \quad (19)$$

$\text{Br}(l) \oplus \frac{1}{2}\text{H}_2 + \frac{1}{2}\text{O}_2 = \text{HBrO}(\text{aq})$ .—Owing to our lack of knowledge of the dissociation constant of hypobromous acid it is impossible to determine the free energy of hypobromite ion. We must therefore at present be content with the determination of that of the free acid. Combining Equations 7, 14 and 19 with Equations 9 and 54 of our paper<sup>2</sup> on the free energy of oxygen and hydrogen compounds, we find

$$\Delta F_{298}^\circ = -19739. \quad (20)$$

$\text{Br}(l) + 3\text{H}_2\text{O}(l) + 5\oplus = 6\text{H}^+ + \text{BrO}_3^-$ .—Sammet<sup>3</sup> measured the potential at 25° of a platinum electrode dipping into an aqueous solution of bromic acid saturated with liquid bromine. He used solutions of  $\text{HBrO}_3$  ranging from 0.001  $M$  to 1.0  $M$ . At present only the results in dilute solutions can be used for exact calculations. Thus the potential in the case of the 0.001  $M$   $\text{HBrO}_3$  against the normal calomel electrode was  $-0.929$  v. By the use of the Planck formula he calculated the liquid potential to be 0.031 v. which is probably as nearly correct as the measurements themselves. The potential therefore against the normal calomel electrode, excluding liquid potentials, is  $-0.960$  v., or against the hydrogen electrode is  $-1.238$  v. We have then the equation  $-1.238 =$

<sup>1</sup> Bray and Connolly, *THIS JOURNAL*, 33, 1485 (1911).

<sup>2</sup> Lewis and Randall, *Ibid.*, 36, 1969 (1914).

<sup>3</sup> Sammet, *Z. physik. Chem.*, 53, 678 (1905).

$E^\circ - RT/5F \ln (H^+)^5(BrO_3^-)$ . Taking the degree of dissociation of 0.001 *M*  $HBrO_3$  as 0.97,

$$E^\circ = -1.487; \Delta F^\circ_{298} = 171550. \quad (21)$$

$Br(l) + \frac{3}{2}O_2 + \ominus = BrO_3^-$ .—Combining Equation 21 with Equations 9 and 54 of our paper on oxygen and hydrogen compounds, we find

$$\Delta F^\circ_{298} = 1690. \quad (22)$$

### Summary.

The following table gives the free energy of formation of the several forms of elementary bromine and of the bromine compounds which have been considered in this paper:

Substance.	$\Delta F^\circ_{298}$ .	Equation.	Substance.	$\Delta F^\circ_{298}$ .	Equation.
$Br(l)$ .....	0	..	$HBr(g)$	-12592	13
$Br_2(g)$ .....	755	1, 2	$Br^-$	-24594	14
$Br(s)$ .....	157	3	$Br_3^-$	-25267	16
$Br_2$ (in $CCl_4$ , $N = 1$ ).....	389	5	$Br_5^-$	-24400	18
$Br_2(aq)$ .....	977	7	$HBrO(aq)$	-19739	20
$Br(g)$ .....	[22328]	10	$BrO_3^-$	1690	22

BERKELEY, CAL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

## THE POTENTIAL OF THE MERCURY ELECTRODE AGAINST MERCUROUS ION.

By G. A. LINHART.

Received September 9, 1916.

One of the lines of work in progress in this laboratory is the accurate measurement of the electrode potentials of the chemical elements. The present paper deals with the determination of the electrode potential of mercury against  $Hg_2^{++}$ .

Ogg<sup>1</sup> has shown, in a qualitative way, that the mercurous ion in a water solution of a mercurous salt, is chiefly in the form of  $Hg_2^{++}$ , and to some extent also in the form of  $Hg^+$ . But for obvious reasons (notably hydrolysis and oxidation) mercurous nitrate is not a suitable substance for accurate electrochemical measurements. Therefore, for the present investigation, mercurous perchlorate was chosen, because it was shown by Ley<sup>2</sup> that the extent to which this salt hydrolyzes is extremely small, and that the small amount of hydrolysis products thus formed are soluble in water. An almost neutral solution of this salt can be prepared, not by reducing the mercuric salt in solution by means of metallic mercury, but by treating pure mercurous oxide with a water solution of pure perchloric acid. The details of preparation, as well as the method of measurements, are given in the experimental part of this paper. In the

<sup>1</sup> Ogg, *Z. physik. Chem.*, **27**, 295 (1898).

<sup>2</sup> Ley, *Z. Electrochem.*, **10**, 302 (1904).

table below are given two typical series of a considerable number of e. m. f. measurements obtained from preliminary experiments of concentration cells of mercurous perchlorate in the presence of perchloric acid of the same concentration throughout the cell. The concentration of the perchloric acid was in all cases in large excess as compared with that of the mercurous perchlorate, so that the degree of dissociation of the latter into  $\text{Hg}_2^{++}$  and  $\text{ClO}_4^-$  was practically the same in the two half cells. Therefore, the e. m. f. of concentration cells in the ratio of 1 : 2 should be 0.0089 v. This, however, is not the case as is evident from the results given in Table I.

TABLE I.—PRELIMINARY RESULTS AT 25°.

Series No.	Conc. of $\text{HClO}_4$ .	Conc. of $\text{Hg}_2(\text{ClO}_4)_2$ .		E (volt).
1.....	0.1035	0.00065	0.0013	0.0093
		0.000325	0.00065	0.0095
		0.0001625	0.000325	0.0097
2.....	0.0207 <sup>1</sup>	0.00065	0.0013	0.0091
		0.000325	0.00065	0.0092
		0.0001625	0.000325	0.0092

The deviations of the e. m. f. values from the theoretical (in this case for a 1 : 2 concentration cell,  $E = 0.0089$  volt) seem to indicate some dissociation of the  $\text{Hg}_2^{++}$  ions into  $\text{Hg}^+$  ions. These deviations were, however, found to be probably due to the method of preparing the perchloric acid, namely, adding the theoretical amount of sulfuric acid to a dilute solution of barium perchlorate. The perchloric acid thus prepared contains a trace of dissolved barium sulfate,<sup>2</sup> in this case it probably contained more sulfate ion than barium ion. It is evident that when this acid is added to two solutions of mercurous perchlorate of different strengths both being extremely dilute, the percentage loss of the mercurous ion from the more dilute solution will be considerably greater than from the more concentrated solution. This phenomenon would account for the regular increase in the e. m. f. in the preliminary results given above. The  $E_0$  calculated from these values would therefore be numerically less than if pure perchloric acid had been used. Many precautions therefore had to be taken in order to obtain accurate results.

The imported perchloric acid used in subsequent experiments proved to be very pure, being prepared presumably by distillation of the acid obtained by heating ammonium perchlorate in the presence of aqua regia.

<sup>1</sup> In this series the e. m. fs. of the concentration cells were measured also against the hydrogen electrode and the values obtained are given below:

$\text{Hg}_2(\text{ClO}_4)_2$ .....	0.0013	0.00065	0.000325	0.0001625 <i>M.</i>
—E.....	0.8055	0.7964	0.7872	0.7780 v.

<sup>2</sup> The solubility of barium sulfate in the presence of perchloric acid is apparently quite appreciable, as on addition of either  $\text{SO}_4^{--}$  or  $\text{Ba}^{++}$  a slight precipitate of  $\text{BaSO}_4$  was observed.

### Experimental.

**Apparatus.**—The hydrogen electrode used is of the type developed in this laboratory, and will be described in a subsequent paper by Prof. G. N. Lewis and Dr. R. L. Sebastian. For the other half cell see Fig. 1.

The cells and separatory funnels previously used in the preliminary experiments were subsequently kept in a cleaning mixture, consisting of fairly pure sulfuric acid saturated with chromic acid, for several weeks, then thoroughly washed, steamed, rinsed with conductivity water,<sup>1</sup> and finally dried in an oven and cooled in a desiccator. The rubber stoppers were boiled in dilute alkali, thoroughly washed and dried. Pure mercury was then introduced into each cell to a depth of about half an inch in order to prevent the solution from coming in contact with the platinum wire beneath the mercury in case of accidental tipping of the cell. The end of the separatory funnel, containing the same solution as the corresponding cell, when inserted into the cell, was almost in contact with the surface of the mercury in order to facilitate the renewal of the solution near the mercury surface.

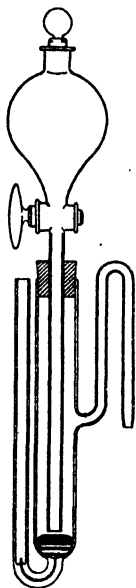


Fig. 1

**Preparation of Substances.**—Starting with pure mercury (twice distilled), pure sodium hydroxide and pure water, pure mercurous oxide was obtained. This was then treated with pure perchloric acid, the excess mercurous oxide filtered out and the solution of mercurous perchlorate thus obtained was shaken with pure mercury and allowed to stand for several days in order that the dispersed mercury could settle out. The solutions were then analyzed<sup>2</sup> and diluted with conductivity water to the desired concentration in specially resistant glass vessels, and then diluted with equal volumes of perchloric acid. These solutions thus prepared were immediately transferred to the cells, treated as described above, and the e. m. f. of each measured against the hydrogen electrode. The acid with which the solutions of the mercurous perchlorate were diluted was exactly twice as concentrated as

<sup>1</sup> Distilled water was redistilled with alkaline permanganate. This kind of water was used in all operations.

<sup>2</sup> 100 cc. of this solution gave, on analysis, 0.2500 g. of mercurous chloride, corresponding to 0.005308 *M* mercurous perchlorate. This solution was diluted and used in the experiments with 0.0118 *M* and 0.0059 *M* HClO<sub>4</sub>. The stock solution used for the other experiments was 0.00550 *M*. Hydrochloric acid was used in the precipitations of the mercurous chloride, giving concordant results with those obtained when sodium chloride was used. Moreover, the filtrate from the sodium chloride precipitations reacted neutral towards litmus paper, showing that there was no excess acid in the mercurous perchlorate, although the original solution of the mercurous perchlorate was slightly acid due to slight hydrolysis.

the acid used in the hydrogen electrode cell and in the connecting vessel forming the liquid junction, so that the concentration of the perchloric acid was the same throughout the cell.

**Electromotive Force Measurements.**—In the first column of Table II is given the number of the series of the e. m. f. measurements; in the second, the concentrations of the perchloric acid in mols per liter of solution; in the third, the concentrations of the mercurous perchlorate in mols per liter of solution; in the fourth and fifth, the observed e. m. fs. of these solutions measured in duplicate against the hydrogen electrode; and in the sixth, the average difference in e. m. f. for a two-fold concentration ratio of the mercurous perchlorate half cells. It may be stated here that the direct measurement of the e. m. fs. of the concentration cells agreed in every case within 0.1 mv. with the differences given in the sixth column.

TABLE II.

Series No.	Conc. of HClO <sub>4</sub> .	Conc. of Hg <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> .	—E.		ΔE (volt).
1.....	0.0817	$\left\{ \begin{array}{l} 0.002750 \\ 0.001375 \end{array} \right.$	0.7777	0.7777	0.0089
			0.7688	0.7688	
2.....	0.0817	$\left\{ \begin{array}{l} 0.000550 \\ 0.000275 \end{array} \right.$	0.7569	0.7568	0.0089
			0.7480	0.7479	
3.....	0.0236	$\left\{ \begin{array}{l} 0.000550 \\ 0.000275 \end{array} \right.$	0.7920	0.7920	0.0089
			0.7831	0.7832	
4(a).....	0.0118	$\left\{ \begin{array}{l} 0.0001062 \\ 0.0000531 \end{array} \right.$	0.7890	0.7889	0.0091
			0.7802	0.7795	
4(b) <sup>1</sup> .....	0.0118	$\left\{ \begin{array}{l} 0.0001062 \\ 0.0000531 \end{array} \right.$	0.7890	0.7889	0.0087
			0.7802	0.7803	
4(c).....	0.0118	$\left\{ \begin{array}{l} 0.0001062 \\ 0.0000531 \end{array} \right.$	0.7889	0.7889	0.0090
			0.7798	0.7800	
5(a).....	0.0059	$\left\{ \begin{array}{l} 0.0001062 \\ 0.0000531 \end{array} \right.$	0.8057	0.8055	0.0089
			0.7970	0.7964	
5(b).....	0.0059	$\left\{ \begin{array}{l} 0.0001062 \\ 0.0000531 \end{array} \right.$	0.8062	0.8061	0.0089
			0.7973	0.7973	

Av., 0.0089

**Discussion of Results.**—No appreciable change in the e. m. f. of Series 1 and 2 (limit of error being 0.05 mv.) could be observed either at the end of one hour or on renewing the solutions near the mercury surface by means of the separatory funnel. In the remaining series, where the concentrations of the perchloric acid were considerably more dilute, the maximum variation in e. m. f. on renewal of the solution was 0.2 mv.,

<sup>1</sup> (b) and (c) denote, respectively, the first and second renewals of the solutions near the mercury surface by means of the separatory funnels.

the limit of error being 0.1 mv. in Series 3 and 4 and 0.2 mv. in Series 5. The same maximum variations were observed also after the cells remained in the thermostat for 30 minutes.

The absence of any consistent departure of the e. m. f. for a two-fold concentration ratio from the theoretical value, 0.0089 v. is evidence that there is no appreciable dissociation of the  $\text{Hg}_2^{++}$  ion into  $\text{Hg}^+$  ion even with 0.00005 molal mercurous perchlorate in 0.006 molal perchloric acid.

**Calculation of the E. M. Fs. in Hypothetical Molal Concentration of the Reacting Substances.**—The reaction taking place at the electrodes may be represented by the following equations:



Whence,

$$E_o = E_{\text{obs.}} + 0.02957 \log \frac{(\text{H}^+)^2}{(\text{Hg}_2^{++})[\text{H}_2]} \quad (3)$$

or

$$E_o = E_{\text{obs.}} + 0.02957 \log \frac{\gamma_1^2(\text{HClO}_4)^2}{\gamma_2(\text{Hg}_2[\text{ClO}_4]_2)[\text{H}_2]} \quad (4)$$

where  $\gamma_1$  denotes the corrected degree of dissociation of  $\text{HClO}_4$  and  $\gamma_2$  that of  $\text{Hg}_2(\text{ClO}_4)_2$ .

Concerning the activity of bivalent ions<sup>1</sup> in solutions of uni-bivalent salts, little information is at present at hand, especially when the uni-bivalent salt, as in the present case, is mixed with a uni-univalent electrolyte. It has been pointed out by Adams and Rosenstein<sup>2</sup> that in a mixture of a bi-univalent salt and a uni-univalent salt, with the same anion, the degree of dissociation (as measured by conductivity) of the former is equal approximately to the square of that of the latter. If we assume provisionally that this is true also of the corrected degree of dissociation, Equation 4 becomes,

$$E_o = E_{\text{obs.}} + 0.02957 \log \frac{(\text{HClO}_4)^2}{(\text{Hg}_2[\text{ClO}_4]_2)[\text{H}_2]} \quad (5)^3$$

If this assumption, which is tested in Table III, were correct, identical values of  $E_o$  would be obtained. As might have been expected, the assumption fails in the most concentrated solutions, but in the three more dilute solutions  $E_o$  is nearly constant, and the average value (0.7926 v.) may be taken as the normal electrode potential of mercury against  $\text{Hg}_2^{++}$  at hypothetical molal concentration.

<sup>1</sup> Lewis and Lacey, *THIS JOURNAL*, 36, 804 (1914).

<sup>2</sup> Linhart, *Ibid.*, 38, 1272 (1916).

<sup>3</sup> The corrections for the barometric pressure of the hydrogen gas amounted to +0.5 mv. in all but the last series of Table III, for which it was +0.6 mv.



TABLE III.

Series No.	HClO <sub>4</sub> . *	Hg <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> .	E <sub>obs.</sub> <sup>1</sup>	E <sub>o</sub> (volt).
1.....	0.0817	{ 0.002750 0.001375	{ 0.77770 0.76880	0.78960 0.78960
				Av., 0.78960
2.....	0.0817	{ 0.000550 0.000275	{ 0.75685 0.74795	0.78945 0.78945
				Av., 0.78945
3.....	0.0236	{ 0.000550 0.000275	{ 0.79200 0.78315	0.79270 0.79275
				Av., 0.79273
4.....	0.0118	{ 0.0001062 0.0000531	{ 0.78893 0.78000	0.79293 0.79290
				Av., 0.79292
5.....	0.0059	{ 0.0001062 0.0000531	{ 0.80588 0.79700	0.79220 0.79220
				Av., 0.79220
Average of Series 3, 4, and 5.....				0.7926

## Conclusions.

(1) The fair agreement of the  $E_o$  values, with the exception of those with 0.0817  $M$  HClO<sub>4</sub>, seem to justify the adoption for dilute solutions o. the rule, proposed by Adams and Rosenstein with reference to the degree of dissociation of bi-univalent salts.

(2) The best value for the potential of the mercurous electrode is —0.7928 v. (av. of Series 3 and 4).

(3) From the e. m. f. measurements of concentration cells no regular deviations from the theoretical value were observed, from which it may be concluded that there is no appreciable dissociation, of Hg<sub>2</sub><sup>++</sup> into Hg<sup>+</sup> even in very dilute solutions with reference both to the perchloric acid (0.0059  $M$ ) and to the mercurous perchlorate (0.0000531  $M$ ).

Finally, I wish to express my indebtedness, for many helpful suggestions, to Professor G. N. Lewis and Doctor E. Q. Adams.

BERKELEY, CAL.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF ARIZONA.]

## THE VANADATES OF BERYLLIUM.

By PAUL H. M.-P. BRINTON.

Received September 8, 1916.

In the course of a general study of vanadates Berzelius<sup>2</sup> prepared what he describes as a yellow, neutral, difficultly soluble, and pulverulent

<sup>1</sup> Averages of  $E_{obs.}$  of Table II.

<sup>2</sup> *Pogg. Ann.*, 22, 58 (1831).

salt, by the addition of ammonium vanadate to a solution of a beryllium salt. He made no analysis of the substance, and assigned no formula. The only other mention of any vanadate of beryllium is made by Tanatar and Kurovski,<sup>1</sup> who by the action of sodium vanadate on beryllium chloride solution obtained a yellow amorphous precipitate which contained 47.28% of  $V_2O_5$ . Another precipitate obtained by using beryllium, nitrate in place of the chloride contained 25.4%  $V_2O_5$  and 46.3%  $BeO$ ; differing from the one before mentioned in being of somewhat lighter color. The compositions of these substances are said to correspond to formulas of the following types:  $xBeCl_2 \cdot yBe_3(VO_4)_2 \cdot zBeO$  and  $xBe(NO_3)_2 \cdot yBe_3(VO_4)_2 \cdot zBeO$ .

During the progress of an investigation<sup>2</sup> of certain general properties of beryllium salts, opportunity was offered for some study of the vanadates of beryllium, and the results of these experiments are here recorded.

A solution of ammonium vanadate, made by dissolving vanadium pentoxide in concentrated ammonium hydroxide and evaporating to small bulk, was added to a dilute solution of beryllium nitrate. The latter was, of course, acid in reaction, owing to hydrolysis, and there was no precipitate on mixing the two solutions. Ammonium hydroxide was added drop by drop until a yellow precipitate formed, and this increased with every drop of the hydroxide. The precipitate, after drying for a week over sulfuric acid in partial vacuum, was analyzed by methods which will be discussed later. The results led to a formula approximately expressed by  $4BeO \cdot V_2O_5 \cdot 6H_2O$ . Subsequent trials in which the conditions of precipitation were varied gave precipitates in which the ratio  $BeO/V_2O_5$  went to about 4.3, while the molecules of water varied from 3.1 to 9.7. It is evident that the products of such precipitations are simply basic mixtures of variable proportions, and do not represent pure compounds.

The ratio 4 for  $BeO/V_2O_5$  differs considerably from that of Tanatar and Kurovski, who obtained a figure of about 13. If they precipitated in the presence of an excess of beryllium salt the variance is easily explained, for my investigations have shown that the ratio of base to acid in such cases can go as high as 60 : 1—in fact, there is no limit to the basicity under these conditions. If the precipitates were obtained in the presence of excess of vanadate the matter is not so easily explained, but in this event it is probable that the difference in composition is due to varying degrees of washing. It was found that the washings from the yellow precipitates, although apparently colorless, none the less contained notable quantities of the vanadate which gave a very distinct yellow color upon concentration by evaporation. From this it is easy to see how the mixtures could become more basic by long-continued washing.

<sup>1</sup> *J. Russ. Phys.-Chem. Soc.*, 41, 813 (1909).

<sup>2</sup> This investigation will be the subject of a later paper.

It was evident that a normal beryllium vanadate was not to be obtained by precipitation with a soluble vanadate, so other means were tried for the preparation of such a compound. With the idea of obtaining an orthovanadate, beryllium hydroxide and vanadium pentoxide were taken in the molecular ratio of 3 : 1. A little of this mixture was boiled with water for an hour, and the yellow solution was filtered from the undissolved residue. Upon cooling the clear yellow filtrate became turbid. Set to evaporate on the water bath, the solution again became clear, and when considerably concentrated it still remained clear after standing in the cold overnight. Evaporation was continued until a deep orange-red, syrupy liquid was obtained, and this, after standing in the cold for two days, set to a solid mass of fascicular crystals. Upon repeating the above experiment with larger quantities of material—6 g. of the mixed oxides, boiled with three successive liters of water—and evaporating to about 40 cc., it took nine days before any separation of crystals took place. At the end of that period the whole had set to a mass of dark yellow crystals, which seemed to get a little darker on standing. The mass was so hard that it was difficult to scratch out a sample with a knife, and it evidently consisted of crystals of two colors, yellow and brown. Upon adding alcohol to some of the crystal mixture the whole surface was converted to a uniform yellow crystal mass.

A rough preliminary analysis of a small portion of the heterogeneous mass indicated that there was probably present a normal metavanadate instead of an orthovanadate, and this metavanadate had either three or four molecules of water of crystallization, as well as a slight excess of beryllium oxide. The analysis was not regarded as very reliable, and it is not worthy of record. It suggested two points, however: that equimolecular weights of the two oxides should be taken to boil together, as that since alcohol was capable of transforming the surface of the heterogeneous mass to fine, yellow crystals, it might be able to precipitate out these yellow crystals from the concentrated syrupy liquid, and these crystals might then be free from basicity.

Equimolecular proportions of beryllium hydroxide and vanadium pentoxide were boiled with water as before, the yellow liquid freed from insoluble residue by filtration, and evaporated to an orange-red syrup. This hot syrup was then poured into a large volume of 95% alcohol. A copious separation of lemon-yellow particles immediately occurred, and after standing twelve hours a thick layer of yellow crystals had settled to the bottom of the dish. Under the microscope the crystals appeared as perfectly homogeneous, yellow, waxy plates. Later attempts in which alcohol was added to a more dilute solution furnished larger crystals of more definite form, and it could then be seen that there were really two sets of crystals; the main mass consisting of particles of about

0.25 mm. average diameter; but scattered among these were a few little flat, tabular crystals, the largest of which did not exceed 0.05 mm. in width or length. These surely did not make up as much as 1% of the total mass. The main crystals are evidently isometric, being cubes modified by an octohedron. The polar angle gives a value of  $54^{\circ} 46'$ , the theoretical value being  $54^{\circ} 44'$ . The cube face in contact with the glass does not show the octohedral modifications. The upper horizontal face is, in nearly all cases, characterized by a quadrangular embayment, or negative development. This feature being developed on only one face of the cube suggests a tetragonal habit, but the values given above for the polar angle seem to prove conclusively that the crystals are isometric. The embayments, then, would appear to result from physical position only, and not from any crystallographic consideration. Thin fragments of these crystals do not polarize light, but the larger tabular crystals, found scattered among the large ones, do polarize light, and seem to show an orthorhombic habit. One of these little crystals was mounted on the goniometer, but, although six faces in the prismatic zone gave signals, they were too irregular to yield satisfactory measurements. For the crystallographic measurements, which were made with a two-circle Goldschmidt goniometer, I am indebted to Prof. F. N. Guild, of the University of Arizona.

Whether or not these very small crystals were the same in substance as the larger ones cannot be said. Making up as small a percentage of the whole as they did, it is certain that they could not have very much effect on the analytical results, and it was physically impossible to isolate enough of the little particles to make an independent analysis of them.

Several batches of the yellow crystals were made at different times, and the following analyses were made on three different lots. The results show clearly that the salt is a normal beryllium metavanadate tetrahydrate, a compound which has not heretofore been prepared.

$\text{Be}(\text{VO}_3)_2 \cdot 4\text{H}_2\text{O}$ .				
	Calculated.	Found.		
BeO.....	9.00	8.44	9.74	9.18
$\text{V}_2\text{O}_5$ .....	65.22	66.60	65.38	66.86
4 $\text{H}_2\text{O}$ .....	25.78	24.96	24.88	23.96

The material represented by the first analysis was crystallized from water, the other two by precipitation with alcohol. The amounts used for analysis in the first two samples were small, and in view of the somewhat unsatisfactory method of separation used, the results are perhaps as concordant as might be expected. The third analysis was made on a good-sized sample, and is in all respects the most reliable. The ratio of  $\text{BeO} : \text{V}_2\text{O}_5$  in this analysis is 1 : 1.002, and this may be taken as con-

clusive proof that we are dealing with a normal metavanadate of beryllium, with four molecules of crystal water, though a little of the latter is evidently lost with comparative ease.

Some difficulty was experienced in finding a method suitable for the exact, quantitative separation of beryllium and vanadium in the scheme for analysis. Attempts to remove the vanadium first, as lead vanadate, were unsuccessful, for it seemed that a concentration of acetic acid sufficient to prevent the co-precipitation of beryllium caused incompleteness in the precipitation of lead vanadate. The method finally adopted was essentially that of Noyes, Bray and Spear.<sup>1</sup> It was, however, necessary to redissolve the first precipitate of basic beryllium carbonate in nitric acid, and to repeat the precipitation under pressure. Occluded sodium salts were removed by again dissolving the basic carbonate in nitric acid, and making final precipitation with ammonium hydroxide. After ignition and weighing, the residue was dissolved in sulfuric acid, and the traces of vanadium determined by titration with permanganate, after reduction by sulfur dioxide. The final filtrate from the beryllium precipitation was treated with sulfuric acid, evaporated to fumes, diluted, reduced by sulfur dioxide, and titrated with potassium permanganate for the determination of the main portion of the vanadium. It should be mentioned that this filtrate was warmed for an hour before the sulfuric acid was added. This treatment usually caused a slight separation of beryllium hydroxide, which was filtered off and added to the main portion. This little precipitate seemed pure white, but if it did contain any vanadium compound this would be corrected for by the determination of the vanadium in the ignited beryllium oxide. The percentage of water of crystallization was taken by difference, having first made sure that there was no alcohol of crystallization.

The approximate solubility of the beryllium metavanadate tetrahydrate was determined by agitation of the fine crystals in a sealed test tube for five days, in a thermostat at 25°. In the filtrate the vanadium was determined by titration, and the solubility thus calculated was found to be one part per thousand of water at this temperature. In hot water the crystals are readily soluble, and on cooling there is a strong tendency toward supersaturation. In pyridine the solubility seems to be of the same order as that in water. The crystals are practically insoluble in chloroform, ether, and absolute alcohol.

The specific gravity of the metavanadate, determined by suspension in methylene iodide diluted with benzene, was found to be 2.273.

The crystals lose water slowly, but continuously, over sulfuric acid, but no definite end point of dehydration could be obtained.

<sup>1</sup> THIS JOURNAL, 30, 481 (1908).

### Summary.

It has been shown that basic mixtures, and not chemical compounds, are obtained by the addition of soluble vanadates to solutions of beryllium salts.

A new compound, beryllium metavanadate tetrahydrate, has been prepared, and its properties described.

TUCSON, ARIZ.

## THE ARSENATES OF LEAD.

[SECOND PAPER.]

### EQUILIBRIUM IN THE SYSTEM $\text{PbO}$ , $\text{As}_2\text{O}_5$ , $\text{H}_2\text{O}$ .

BY C. C. McDONNELL AND C. M. SMITH.

Received October 4, 1916.

In a preceding article<sup>1</sup> we showed that trilead arsenate, although spoken of freely in the literature, is not so easily produced as is ordinarily believed. Double decomposition between soluble lead salts and soluble arsenates rarely gives a product of theoretical composition, and the action of excess ammonia on dilead arsenate leads to the formation of a basic compound, as was first recorded by Tartar and Robinson.<sup>2</sup> These facts suggested that trilead arsenate is relatively unstable and capable of existing only under very limited conditions. In order to clear up this point the following phase rule study was undertaken.

The three component system  $\text{PbO}$ ,  $\text{As}_2\text{O}_5$  and  $\text{H}_2\text{O}$  can easily be investigated as far as mono- and dilead arsenates are concerned, but the system as such cannot be followed beyond dilead arsenate, owing to the insolubility of lead hydroxide. This necessitates the use of some other base to produce alkalinity. Ammonia seemed particularly suitable for this purpose, since it is easily prepared free from carbon dioxide, has practically no solvent action on lead compounds, and does not form double salts under conditions such as obtained in these experiments. Then, too, it is of especial interest since its action on dilead arsenate has long been considered the best means of producing trilead arsenate, as first stated by Berzelius.<sup>3</sup>

The use of ammonia in such a system introduces a fourth component, but by keeping its concentration constant one degree of freedom is destroyed, and the system will behave like a three-component one. (Owing to the low concentrations employed, we are justified in the assumption that the volume changes were nil or insignificant.)

The experiments were carried out in the following manner: Pure ammonia water was prepared (by distilling concentrated C. P. ammonia water over barium hydroxide to remove  $\text{CO}_2$ , and absorbing the evolved

<sup>1</sup> THIS JOURNAL, 38, 2027 (1916).

<sup>2</sup> *Ibid.*, 36, 1848 (1914).

<sup>3</sup> *Ann. chim. phys.*, [2] 11, 229 (1819).

vapors in recently boiled and cooled distilled water) and diluted to 0.0338 *N* (arbitrary dilution). A series of 2 g. portions of pure amorphous dilead arsenate,  $\text{PbHAsO}_4$ , were put into flasks, and to them were added varying amounts, from 90 to 180 cc., of the dilute ammonia solution.

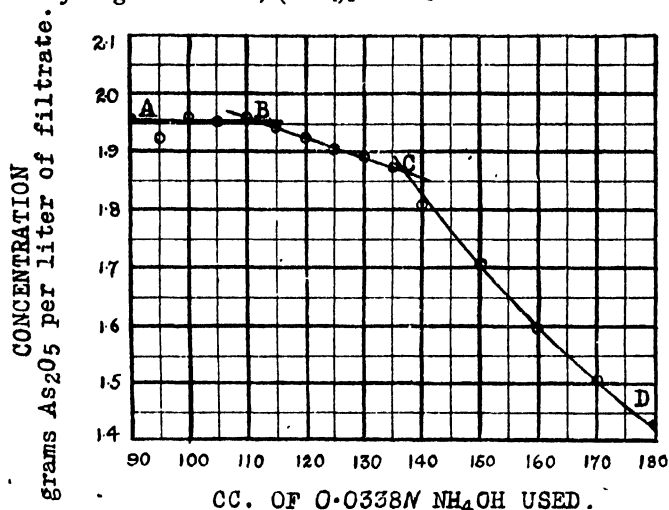
All of the mixtures were put into a shaking machine and agitated for seven hours on each of two successive days at  $32^\circ \pm 1^\circ$ . (It was determined that equilibrium had been reached in this time.) After allowing the mixtures to settle, they were filtered on Gooch crucibles containing disks of filter paper and the clear filtrates analyzed. The results showed that only a mere trace of lead went into solution, but a considerable amount of arsenic, indicating that the reaction consisted in the removal of a portion of the arsenic acid from the dilead arsenate to form soluble ammonium arsenate. The course of the reaction could, therefore, be followed by determining the arsenic oxide in solution, the results of which are here tabulated.

Cc. of 0.0338 <i>N</i> $\text{NH}_4\text{OH}$ used.	G. of $\text{As}_2\text{O}_5$ per liter of filtrate.	Total g. of $\text{As}_2\text{O}_5$ dissolved.
90	1.956	0.1760
95	1.925	0.1829
100	1.960	0.1960
105	1.953	0.2051
110	1.960	0.2156
115	1.941	0.2232
120	1.926	0.2311
125	1.902	0.2378
130	1.891	0.2459
135	1.871	0.2526
140	1.809	0.2533
150	1.706	0.2559
160	1.591	0.2546
170	1.503	0.2555
180	1.429	0.2572

The significance of these results is brought out more clearly in the accompanying graph.

The first additions of ammonia have resulted in the formation of a constant solution, as shown by the branch A-B of the graph, which, in a three-component system at constant temperature, indicates the existence of two solid phases. One of these must, of course, be the unchanged dilead arsenate, and the other may easily be determined as follows: The constant solution contains 1.951 g.  $\text{As}_2\text{O}_5$  per liter, and the break B in the graph occurs at 112 cc., making the total dissolved  $\text{As}_2\text{O}_5 = 0.2185$  g. The transposition of 2 g. of dilead arsenate to trilead arsenate requires the solution of 0.2208 g.  $\text{As}_2\text{O}_5$ . The molecular ratio of the residue,  $\text{PbO}/\text{As}_2\text{O}_5$ , figures out as 2.99, showing that trilead arsenate is the second solid phase. Analysis of the residues immediately preceding and following the point B gave 25.65 and 25.31%  $\text{As}_2\text{O}_5$ , respectively,

while the formula  $\text{Pb}_3(\text{AsO}_4)_2$  requires 25.56%, which is additional confirmation that it is trilead arsenate. The constant solution (to the point B) contains 0.00849 mol.  $\text{As}_2\text{O}_5$  per liter, making the molecular ratio  $\text{NH}_4\text{OH}/\text{As}_2\text{O}_5 = 3.98$ , which is practically equivalent to a solution of diammonium hydrogen arsenate,  $(\text{NH}_4)_2\text{HAsO}_4$ .



The portion B-C of the graph shows why trilead arsenate is not ordinarily obtained by double decomposition. If, after all the dilead arsenate was changed to the tri-salt, the latter remained as such on adding more ammonia, the total dissolved  $\text{As}_2\text{O}_5$  would remain constant and the graph become a rectangular hyperbola. But a continued increase is shown in the total  $\text{As}_2\text{O}_5$  dissolved and the branch B-C is a straight line. This indicates the formation of a series of solid solutions, with trilead arsenate as one end member and some basic arsenate as the other. At the point C 0.2553 g. of  $\text{As}_2\text{O}_5$  has been dissolved, leaving in the residue 0.407 g.  $\text{As}_2\text{O}_5$  and 1.286 g.  $\text{PbO}$ , giving a molecular ratio  $\text{PbO}/\text{As}_2\text{O}_5 = 3.253$ .

Beyond the point C, the total dissolved  $\text{As}_2\text{O}_5$  remains practically constant, and the graph then becomes a rectangular hyperbola, showing that this basic arsenate is not further changed within the limits of our experiments. A large excess of ammonia water produces a product only slightly more basic, having a molecular ratio about 3.30.

About 100 g. of trilead arsenate were prepared by treating dilead arsenate with the theoretical amount of  $N/10$  ammonia, as calculated from the foregoing data. Analysis:

	Dried at 110°.	Anhydrous.	Theory for $\text{Pb}_3(\text{AsO}_4)_2$ .
Lead oxide, $\text{PbO}$ .....	73.62%	74.30%	74.44%
Arsenic oxide, $\text{As}_2\text{O}_5$ .....	25.46%	25.70%	25.56%
Water (by ignition).....	0.92%	.....	.....
	100.00%	100.00%	100.00%



The product contains a small amount of water which is not expelled at 110°. This corresponds to slightly less than  $\frac{1}{2}$  molecule. It is an amorphous powder, with a specific gravity,  $15/4$  of 7.00. Crystallized trilead arsenate (anhydrous) prepared by fusion, had a specific gravity  $15/4$  of 7.30.

### Summary.

It has been shown that the action of dilute ammonia on dilead orthoarsenate proceeds as follows:

(1) Transposition to trilead orthoarsenate,  $Pb_3(AsO_4)_2$ , the supernatant solution remaining constant at the  $(NH_4)_2HASO_4$  stage until transformation is complete.

(2) Formation of solid solutions ranging from trilead arsenate to a basic arsenate, beyond which no further change occurs.

INSECTICIDE AND FUNGICIDE LABORATORY,  
MISCELLANEOUS DIVISION, BUREAU OF CHEMISTRY,  
WASHINGTON, D. C.

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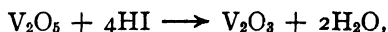
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF VIRGINIA.]

## THE REDUCTION OF VANADIC ACID BY HYDRIODIC ACID.

By GRAHAM EDGAR.

Received August 28, 1916.

In a recent paper by Ditz and Bardach<sup>1</sup> experimental results are given which indicate that the reduction of vanadic acid by hydriodic acid at room temperature and at considerable dilution proceeds irregularly, and that the iodine liberated in the course of the reaction corresponds approximately to that calculated for the reaction



or in some instances to an even greater amount. At the same time it is pointed out that tetravalent vanadium is relatively stable towards dilute hydriodic acid. In order to explain their results, Ditz and Bardach offer the hypothesis that the reduction of vanadic acid by hydriodic acid proceeds directly from the pentavalent to the trivalent state, without the formation of tetravalent vanadium as an intermediate product.

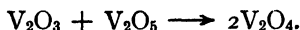
The results of Ditz and Bardach conflict with those of several earlier investigators. Numerous statements occur in the literature to the effect that reduction of vanadic acid by dilute hydriodic acid proceeds until the vanadium approximates the *tetravalent* condition,<sup>2</sup> and several investigators have defined conditions under which a quantitative reduction may be expected, and have based methods for the estimation of vanadium

<sup>1</sup> *Z. anorg. Chem.*, **93**, 97 (1915).

<sup>2</sup> Browning, *Am. J. Sci.*, [4] **2**, 185 (1896); Hett and Gilbert, *Z. öffentl. Chem.*, **12**, 265 (1906); Warynski and Mdivani, *Mon. Sci.*, **22**, II, 527 (1908); Perkins, *Am. J. Sci.*, [4] **29**, 540; Rosenheim, *Inaug. Diss. Berlin* (1888).

upon the reaction.<sup>1</sup> The experimental conditions in most cases seem more favorable for reduction than those described by Ditz and Bardach.

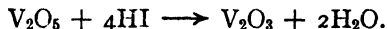
Furthermore it is stated by Rutter<sup>2</sup> that trivalent and pentavalent vanadium react with one another readily in acid solution, undergoing mutual oxidation and reduction in the sense of the equation



If this is true, then reduction of vanadic acid by hydriodic acid *must* pass through the tetravalent stage, even if the initial reduction involved the formation of trivalent vanadium, and since tetravalent vanadium is relatively stable towards dilute hydriodic acid,<sup>3</sup> further reduction must proceed with great difficulty.

The conclusions of Ditz and Bardach seem, therefore, to warrant further investigation.

The experiments described by them are essentially as follows: (1) About 0.062 g. of vanadic acid (in solution as ammonium vanadate) was measured into a large bottle fitted with a separatory funnel and a trap valve. To it were added 1000 cc. of water, 75 cc. of conc. HCl, and 1.5 g. of KI. After vigorous shaking the bottle was allowed to stand for a few minutes and then titrated for iodine with dilute  $\text{Na}_2\text{S}_2\text{O}_3$  solution, after the addition of starch. After the first titration the bottle was allowed to stand, and the continually reappearing blue color of "starch-iodide" was removed from time to time by further titration with thiosulfate. After several hours the amount of thiosulfate used corresponded in most cases to somewhat *more* than that calculated on the assumption that the reduction had proceeded according to the equation



(2) A solution containing  $\text{V}_2\text{O}_5$ , HCl and KI in approximately the same concentrations as in the preceding experiments was shaken repeatedly in a separatory funnel with toluene, and the combined toluene extracts were titrated with thiosulfate as before. Here again the amount of thiosulfate used corresponded to a quantity of iodine somewhat greater than that calculated on the assumption that the reduction had proceeded until the vanadium was in the trivalent condition.

An obvious source of possible error in these experiments is that of atmospheric oxidation. This is indeed admitted by Ditz and Bardach, but they do not seem to consider that this error can materially influence the results. In the present paper experiments are described which cover almost the same ground as those of Ditz and Bardach, but the influence

<sup>1</sup> Browning, *Am. J. Sci.*, [4] 2, 185 (1906); Warynski and Mdivani, *Mon. Sci.*, 22, II, 527 (1908); Perkins, *Am. J. Sci.*, [4] 29, 540.

<sup>2</sup> *Z. anorg. Chem.*, 32, 368 (1907).

<sup>3</sup> Ditz and Bardach, *Z. anorg. Chem.*, 93, 97 (1915); Muller and Diefenthaler, *Z. anal. Chem.*, 51, 21 (1912); Wegelin, *Ibid.*, 53, 80 (1914).

of atmospheric oxidation has been kept as low as possible, and very different results have been obtained in consequence.

### Experimental.

Solutions of sodium vanadate, sodium thiosulfate, and iodine, each approximately 0.05 *N* were prepared and carefully standardized. An apparatus similar to that of Ditz and Bardach was prepared for the preliminary experiments. It consisted of a large bottle (Fig. 1) fitted with a tightly fitting paraffined cork, through which passed a separatory funnel, a trap valve, and a bent glass tube through which a current of carbon dioxide could be passed.

In the first experiment there were placed in the bottle 1000 cc. of distilled water, 75 cc. of conc. HCl, and about 0.1000 g. of  $V_2O_5$  (added as sodium vanadate). The trap was charged with 10 cc. of 5% KI solution. Then a current of carbon dioxide was passed for some time through the solution to remove air from the bottle and to diminish the amount of dissolved oxygen. After the gas had been passed through the liquid for about 30 minutes, 30 cc. of 5% KI were added from the funnel, and the current of  $CO_2$  was discontinued. At the end of an hour's time, starch was added and the solution was titrated with 0.05 *N* (approx.) thiosulfate solution, still without admission of air. This titration required 23.15 cc. of thiosulfate solution (calculated for reduction to *tetravalent* vanadium, 24.20 cc.). After a few minutes the blue color returned, and was discharged by the addition of more thiosulfate. This was repeated three times during the next six hours, resulting in a total consumption of 28.35 cc. of thiosulfate for all titrations. After the last titration the blue color of "starch-iodide" had not returned after *three days'* standing, thus exhibiting no further signs of reduction. At the end of that time the bottle was opened and air admitted, and after a few hours the blue color due to iodine had developed again.

In this experiment the amount of thiosulfate used corresponds to somewhat more than that calculated from the assumption that the reduction proceeds only to the tetravalent condition, but the evidence that this excess was caused largely at least by atmospheric oxidation seemed so strong that a set of experiments was devised to study the reaction under conditions more readily controlled.

For this purpose the apparatus shown in Fig. 2 was constructed. It consisted of a large separatory funnel (about 550 cc.) connected by means of a ground glass connection with a small separatory funnel, and a glass tube through which a gas could be admitted. The figure shows the de-

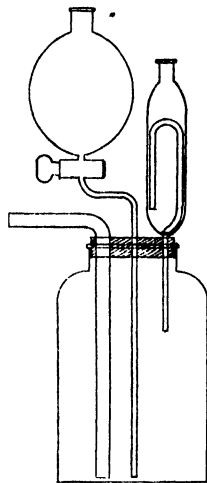


Fig. 1.

tails clearly. The technique involved in carrying out the experiments in this apparatus was as follows: The desired amounts of sodium vanadate

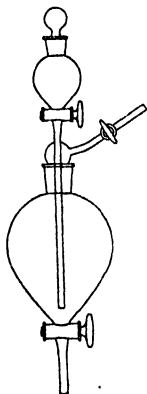


Fig. 2.

solution, concentrated hydrochloric acid, and distilled water were run into the apparatus through the small separatory funnel, and a current of pure hydrogen gas was then bubbled through the liquid for about twenty minutes in order to remove air as far as possible. At the end of this time the desired amount of 5% potassium iodide solution was run in through the small funnel, and this was followed by 25 cc. of pure carbon bisulfide. All stopcocks were then closed, and the apparatus was shaken vigorously from time to time for perhaps half an hour. The carbon bisulfide was then drawn off through the lower stopcock, while hydrogen was admitted from the upper one. A fresh portion of carbon bisulfide was then admitted through the small separatory funnel, and the shaking was repeated as before.

This process was continued until fresh portions of carbon bisulfide failed to extract any further amount of iodine even after standing for several hours. The time necessary for the reaction to become complete varied with the concentration of the different reagents, but was never less than an hour and a half nor greater than four hours. In all cases the apparatus was allowed to stand for twelve hours after apparent completion of the reaction, in order to make sure that no further separation of iodine took place, and in one case, after six weeks' standing under hydrogen, no further separation of iodine could be observed. The combined carbon bisulfide extracts were carefully titrated for iodine with 0.05 *N* sodium thiosulfate solution. The results of the experiments are given in Tables I and II. In Table I the concentration of reagents are approximately the same as those employed by Ditz and Bardach; in Table II the effect of certain variations in the concentrations has been studied.

TABLE I.

Total volume of solution in every case  
500 cc. containing 0.06379  $V_2O_5$ .

Cc. conc. HCl.	Cc. 5 % KI.	Cc. 0.05 <i>N</i> $Na_2S_2O_4$ .	Cc. calc. for reduction to $V_2O_4$ .
37.5	15	14.10	14.00
37.5	15	14.05	14.00
37.5	15	14.20	14.00
37.5	15	14.10	14.00
37.5	15	14.10	14.00
37.5	15	14.05	14.00

TABLE II.

Total volume of solution in every case  
500 cc. containing 0.0637 g.  $V_2O_5$ .

Cc. conc. HCl.	Cc. 5 % KI.	Cc. 0.05 <i>N</i> $Na_2S_2O_4$ .	Cc. calc. for reduction to $V_2O_4$ .
37.5	30	14.20	14.00
37.5	30	14.15	14.00
37.5	60	14.15	14.00
75.0	15	14.05	14.00
75.0	15	14.10	14.00
110.0	15	14.15	14.00

The results given in Table I under conditions of concentration of acid and iodide almost identical with those used by Ditz and Bardach, show that the iodine liberated in the reaction corresponds almost exactly with

that calculated for reduction of the vanadium to the *tetravalent* condition, and not to that calculated for reduction to the *trivalent* condition, as found by Ditz and Bardach. Furthermore the color of the solution at the conclusion of the experiment was in every case the pure blue of tetravalent vanadium, and not the green trivalent. Obviously the large amounts of iodine which Ditz and Bardach found to be liberated in their experiments were caused partially by atmospheric oxidation. Further proof of this was given by an experiment carried out with the same concentration of reagents as those in Table I, and with the same technique, except that the air in the apparatus was not removed by hydrogen. In this case the amount of thiosulfate required for titration of the iodine after four hours' repeated extraction with  $\text{CS}_2$  was 21.20 cc., an excess of 50+ % over that found necessary for the titrations given in Table I. Table II contains the results of experiments carried out with the same technique as that employed in the experiments of Table I, but the concentrations of acid have been varied in such a direction as to make the conditions more favorable for reduction than those studied in the previous experiments. The results show that even if the concentration of acid is made three times that employed by Ditz and Bardach, or if the concentration of iodide is increased to four times that used in their experiments, the amount of iodine liberated corresponds closely to that calculated for reduction of the vanadium to the tetravalent condition. Moreover, the solution at the completion of the experiment has the blue color of tetravalent vanadium, as in the experiments of Table I. The only noticeable effect caused by changing the concentrations of acid and iodide was that the time necessary for the reaction to come to completion was materially shortened by an increase in the concentration of either acid or iodide. The effect of the acid was more marked than that of the iodide, possibly because of the fact that carbon bisulfide does not extract the iodine as efficiently from a concentrated iodide solution as from a dilute one, and, therefore, the removal of the iodine from the solution was not so complete as in the experiments in which the acid concentration was high and that of the iodide low.

Some explanation seems necessary for the large increase in the amount of iodine liberated when air is admitted into the apparatus. Blank experiments carried out with dilute hydrochloric acid and potassium iodide, but without the  $\text{V}_2\text{O}_5$ , showed that a little iodine is liberated when the solution is shaken with  $\text{CS}_2$  in the presence of air but the amount is not nearly large enough to explain the results obtained in the presence of pentavalent vanadium under the same conditions. Likewise blank experiments carried out in the presence of tetravalent vanadium (previously prepared by reduction of pentavalent vanadium with sulfur dioxide) failed to show appreciable liberation of iodine after a few hours' extraction

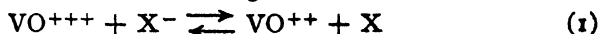
with  $\text{CS}_2$  in the presence of air. Ditz and Bardach, in attempting to account for the fact that they found more iodine liberated than corresponded to reduction of the vanadium to the trivalent condition, offer the following explanation: (1) Pentavalent vanadium is reduced directly to the trivalent condition by dilute hydriodic acid; (2) in the presence of air the trivalent vanadium is oxidized to something (probably not tetravalent vanadium) which reacts further with the hydriodic acid to cause liberation of iodine. This explanation seems cumbersome and unnecessary. In the first place, the results given in this paper show that under the conditions of experimentation the iodine liberated corresponds to that calculated for formation of tetravalent vanadium, and the color of the solution is evidence that tetravalent vanadium is actually formed. There is no evidence that trivalent vanadium is formed, nor does it seem probable from the theoretical standpoint. A simpler and more plausible explanation of the excess of iodine liberated in the presence of air, is that pentavalent vanadium acts as a catalyst in accelerating the oxidation of hydriodic acid by the oxygen of the air, as certain other oxidizing agents are known to do.

Altogether there seems no reason to suppose that the nature of the reaction of hydriodic acid with pentavalent vanadium differs essentially from the similar reactions with the other halogen acids, or that tetravalent vanadium is not the primary product of reduction. This will be discussed further below.

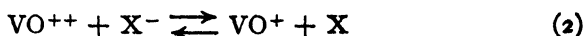
#### The Mechanism of the Reduction of Vanadic Acid by the Halogen Acids.

Numerous investigators have studied the reactions between the halogen acids and vanadic acid, and the apparent conflict between their results has in some cases led to considerable controversy. In view of the fact that even in some recent papers there appears to be some misconception of the mechanism of the reactions, and of the function of the different reacting substances, it may be well to give a brief discussion of the subject from the standpoint of the theory of electronic oxidation and reduction,<sup>1</sup> and to show how some of the conflicting views may be reconciled.

The most logical method of representing the reaction between vanadic acid and the halogen acids is the following:



and similarly for further reduction



where X represents the halogen (Cl, Br or I).

Obviously conditions which favor the progress of Reaction 1 from left to right are: (a) high concentration of the halogen ion; (b) high concentration of the  $\text{VO}^{+++}$  ion; (c) low discharging potential of the halogen

<sup>1</sup> Stieglitz, *Qual. Anal.*, Vol. I, p. 251.

ion; and (d) removal of the product of the reaction, X, from the solution (usually by boiling, by evaporation, by extraction, or by reaction with a metal).

Similar conditions will likewise favor the progress of Reaction 2.

The concentration of the halogen ion can of course be varied at will, and the discharging potential (c) will vary with the particular halogen used, being greatest with chlorine and lowest with iodine.

The concentration of positively charged vanadium ions ( $V^{++\cdot++}$ , or more correctly,  $VO^{++\cdot+}$ ) will depend almost entirely upon the hydrogen ion content of the solution. Just as in the case of any other element whose oxide exhibits amphoteric properties the acidic ionization of vanadic acid will be diminished and its basic ionization increased, by increasing the hydrogen ion content of the solution.

Bearing these four different factors in mind, and their influence on the reaction, the apparent conflict in the results of different investigators is readily explained.

**Reduction by Hydrochloric Acid.**—In this case we have to overcome the high discharging potential of the chlorine ion, and for complete reduction of pentavalent vanadium to tetravalent all of the other factors mentioned above must be favorable. Thus dilute hydrochloric acid is practically without reducing action upon vanadic acid solutions<sup>2</sup> and even the ordinary process of boiling vanadic acid with concentrated hydrochloric acid<sup>3</sup> fails to produce completion of Reaction 1.<sup>4</sup> It is only when the highest concentration of hydrogen ion and halogen ion is maintained<sup>5</sup> or when the solution is repeatedly evaporated to dryness with concentrated acid,<sup>6</sup> that complete reduction can be effected. Even then the results are not always of the highest degree of uniformity.<sup>7</sup> In no case do we have evidence that Reaction 2 takes place even to the slightest extent.

**Reduction by Hydrobromic Acid.**—In this case the discharging potential is much lower than in the case of the chlorine ion, and in consequence reduction takes place more readily. Thus it has been shown that for solutions whose hydrogen ion content is rather high (4–6 molar) the concentration of bromine ion need not be excessive to effect complete reduc-

<sup>1</sup> Ephraim, *Z. anorg. Chem.*, **35**, 66 (1903); Dullberg, *Z. physik. Chem.*, **45**, 129 (1903).

<sup>2</sup> Ditz and Bardach, *Z. anorg. Chem.*, **93**, 97 (1915).

<sup>3</sup> Berzelius, *Pogg. Ann.*, **22**, 49 (1831); Bunsen, *Ann.*, **86**, 305 (1853); Gibbs, *Am. Chem.*, **J.**, **5**, 370 (1883).

<sup>4</sup> Milch, *Inaug. Diss. Berlin* (1887); Holverscheid, *Ibid.* (1890); Rosenheim, *Ibid.* (1888); Gooch and Stookey, *Am. J. Sci.*, [4] **14**, 369 (1902).

<sup>5</sup> Gooch and Stookey, *Am. J. Sci.*, [4] **14**, 369 (1902); Bèard, *Ann. chim. anal.*, **10**, 41 (1905).

<sup>6</sup> Campagne, *Ber.*, **36**, 3164 (1903); Auchy, *J. Ind. Eng. Chem.*, **1**, 455 (1907).

<sup>7</sup> Muller and Diefenthaler, *Z. anal. Chem.*, **51**, 21 (1912).

tion of pentavalent vanadium to the tetravalent condition, provided the bromine is removed from the solution by boiling.<sup>1</sup> If the acid concentration is still higher, Reaction 1 goes to completion with relatively low concentration of bromine ion, even at room temperature.<sup>2</sup> Several accurate volumetric processes for the estimation of vanadium have been based upon this reaction, as there is a rather wide range of conditions under which Reaction 1 goes to completion, and Reaction 2 does not begin to take place. On the other hand, if *all* of the factors influencing reduction are made favorable (for example, by boiling vanadic acid with concentrated hydrobromic acid, in which *both* hydrogen and bromine ion are present in very high concentration) Reaction 2 begins to take place, and a considerable amount of trivalent vanadium may be formed.<sup>3</sup>

**Reduction by Hydriodic Acid.**—It is in this case that much of the difference of opinion in regard to the reaction of vanadic acid with the halogen acids is found. Methods for the quantitative estimation of vanadium have been proposed, based upon the reduction of vanadium from pentavalent to tetravalent condition,<sup>4</sup> from pentavalent to trivalent condition,<sup>5</sup> and from tetravalent to trivalent condition<sup>6</sup> by the action of hydriodic acid under various conditions. On the other hand, numerous investigators have obtained very irregular results with the reaction, and have raised objections to its use for quantitative purposes.<sup>7</sup> This is probably partially due to failure to eliminate the error due to atmospheric oxidation of the acid iodide solutions, and partially to the fact the range of conditions under which Reaction 1 is complete and Reaction 2 not occurring is more limited than in the case of the reduction involving hydrobromic acid. A careful study of the literature shows that if the concentration of hydrogen ion is kept moderate and that of the iodide ion small, reduction of pentavalent vanadium to tetravalent takes place readily, if the iodine set free is removed by boiling,<sup>8</sup> by extraction with a solvent (see above), or by reaction with a metal.<sup>9</sup> Oxidation of the acid iodide solution must be

<sup>1</sup> Holverscheid, *Inaug. Diss. Berlin* (1890); Gooch and Curtis, *Am. J. Sci.*, [4] 17, 41 (1904); Bèard, *Ann. chim. anal.*, 10, 41 (1905).

<sup>2</sup> Ditz and Bardach, *Z. anorg. Chem.*, 93, 97 (1915).

<sup>3</sup> Gooch and Curtis, *Am. J. Sci.*, [4] 17, 41 (1904).

<sup>4</sup> Browning, *Am. J. Sci.*, [4] 2, 185 (1896); Warynski and Mdivani, *Mon. Sci.*, 22, II, 527 (1908); Perkins, *Am. J. Sci.*, [4] 29, 540.

<sup>5</sup> Friedheim and Euler, *Ber.*, 28, 2067 (1895).

<sup>6</sup> Edgar, *Am. J. Sci.*, [4] 27, 174 (1908); Friedheim and Euler, *Ber.*, 28, 2067 (1895).

<sup>7</sup> Ditz and Burdach, *J. anorg. Chem.*, 93, 97 (1915); Gooch and Curtis, *Am. J. Sci.*, [4] 17, 41 (1904); Mülle rand Diefenthaler, *Z. anal. Chem.*, 52, 11 (1912); Wegelin, *Ibid.*, 53, 80 (1914); Ditte, *Compt. rend.*, 102, 1310 (1886); Rosenheim, *Inaug. Diss. Berlin* (1888).

<sup>8</sup> Browning, *Am. J. Sci.*, [4] 2, 185 (1896); Gooch and Curtis, *Ibid.*, [4] 17, 41 (1904); Warynski and Mdivani, *Mon. Sci.*, 22, II, 527 (1908).

<sup>9</sup> Perkins, *Am. J. Sci.*, [4] 29, 540.



guarded against and the proper conditions carefully observed, however, if accurate results are to be obtained. Further reduction of the tetravalent vanadium to trivalent (Reaction 2) does not take place appreciably in solutions in which the concentrations of hydrogen and iodide ion are kept low, but it is possible by making these two factors favorable to effect a complete reduction of tetravalent to trivalent vanadium.<sup>1</sup> Naturally, pentavalent vanadium can be reduced to trivalent by the use of high concentrations of acid and iodide,<sup>2</sup> but the evidence does not justify the assumption that the tetravalent condition is not reached as an intermediate stage. The conditions for effecting a quantitative reduction must be more sharply defined than in the case of hydrobromic acid, but there seems to be no evidence that the mechanism of the reaction is different from that occurring in the case of the other halogen acids.

### Summary.

(1) The reaction between vanadic acid and hydriodic acid at room temperature and at considerable dilution has been investigated. Within the limits of concentration covered by this investigation the reaction results in the formation of tetravalent vanadium, and not trivalent. This is contrary to the observations of Ditz and Bardach. A probable source of error in the results of Ditz and Bardach has been pointed out.

(2) The mechanism of the reactions between vanadic acid and the halogen acids, and the influence of various factors upon the equilibrium, has been discussed.

CHARLOTTESVILLE, VA.

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[COMMUNICATION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA.]

## ANALYSIS OF CERTAIN TUNGSTEN DERIVATIVES.

BY ORLAND R. SWEENEY.

Received September 20, 1916.

The analysis of "complex inorganic acids" and their salt derivatives has been a subject of interest to analysts. Peculiar difficulties have been frequently encountered, and the impression exists that none of the methods proposed for the various separations are satisfactory. In passing, it may be observed that these doubts are particularly strong in connection with the separation of phosphoric and vanadic acids from molybdic and tungstic acids. In this laboratory where, for many years, "complexes" have received attention, numerous opportunities have arisen to test the proposals made from time to time, and as it was given me to inquire more closely

<sup>1</sup> Gooch and Curtis, *Am. J. Sci.*, [4] 17, 41 (1904); Friedheim and Euler, *Ber.*, 28, 2067 (1895); Edgar, *Am. J. Sci.*, [4] 27, 174 (1908).

<sup>2</sup> Gooch and Curtis, *Am. J. Sci.*, [4] 17, 41 (1904); Friedheim and Euler, *Ber.*, 28, 2067 (1895).

into some of these problems, I submit personal experiences with certain of these derivatives. I tried first of all to separate arsenic from tungstic acid; the acids being in the form of their sodium salts. Since arsenic acid may be completely volatilized from its salts, if the latter are exposed, at a comparatively low heat, to the action of dry hydrogen chloride gas, it seemed that in a mixture of sodium pyroarsenate and sodium tungstate this course would lead to a prompt and complete elimination of the arsenic acid. Accordingly weighed portions of sodium arsenate and sodium tungstate were exposed in a boat, to a stream of hot hydrogen chloride. The tungstate was immediately attacked, giving variously colored products, depending upon the temperature. It was found, however, that the arsenic, in the presence of the tungstate, was completely expelled only with great difficulty.

Numerous experiments were made to determine the temperature at which a complete separation could be effected. The results showed that the temperature at which it was practical to remove the arsenic acid was dangerously near the point at which the tungstic acid began to volatilize.

Since only a small amount of the tungstic acid volatilized at  $300^{\circ}$  (measured by a thermometer lying at the side of the combustion tube), it was thought best to collect the portion which volatilized, rather than try to regulate the temperature in such a manner as to completely prevent it. By working in this way the arsenic acid was fully removed to a suitable receiver in four hours. The contents of the combustion tube were rinsed into an evaporating dish with dilute ammonia and evaporated to dryness on the water bath. The residue was then digested with 1 : 1 nitric acid, while small quantities of hydrochloric acid were added from time to time. When all action had ceased the watch-glass cover was rinsed off, and the liquid was evaporated. The residue was moistened with nitric acid and evaporated several times to remove all chlorine. The residue, consisting of tungsten trioxide and sodium nitrate, was dissolved in sodium hydroxide, diluted and filtered. A few drops of methy orange were added, and the solution was just neutralized with nitric acid. It was then boiled, cooled, and the tungstic acid precipitated with mercurous nitrate. After standing four hours it was filtered, washed with 2% mercurous nitrate, and ignited and weighed as tungsten trioxide.

The method of evaporating with nitric acid, and then filtering out the tungsten trioxide, always gave low results. The procedure described—which is really an adaptation of Smith and Exner's method of getting pure tungsten trioxide—gave splendid results. In operating with "complex" salt, such as sodium arsenio-tungstate, a weighed portion was brushed into a small tube, open at both ends, and distributed by rolling and tapping. This tube was then placed in a combustion tube and exposed to a stream of dry hydrogen chloride for about an hour. The

temperature, as measured by a thermometer lying at the side of the combustion tube, was about  $200^{\circ}$ . Since, however, the temperature within the tube varied somewhat with the construction of the apparatus, the proper temperature was ascertained by turning the flames gradually higher until the tungstic acid began to volatilize, and condense on the tube, over the sample; a few degrees lower than this seemed to be the proper temperature to use. With this point determined, the wing-top burners were left permanently adjusted, the gas being regulated at the gascock.

After an hour the apparatus was cooled, the inner tube removed, the sample moistened with water, the tube replaced, and the gas passed for one-half hour longer. This precaution was repeated three times.

Then the receiver was disconnected and the contents of the combustion tube were rinsed into it after first withdrawing the inner tube. A second receiver was put in place, the sample again moistened and the operation repeated. Should the contents of the second receiver show the presence of arsenic when treated with hydrogen sulfide, the treatment must be repeated. The following results were obtained:

Sample of arsenio-tungstate.	Percentage $\text{As}_2\text{O}_3$ .	Percentage $\text{WO}_3$ .
0.1028 g.	11.63	71.01
0.1550 g.	11.57	70.83
0.2858 g.	11.77	70.88
0.2090 g.	.....	71.10
0.1409 g.	11.93	70.76
0.2788 g.	11.93	70.91

The method is then satisfactory and does not require a longer time for its execution than many other procedures in general use.

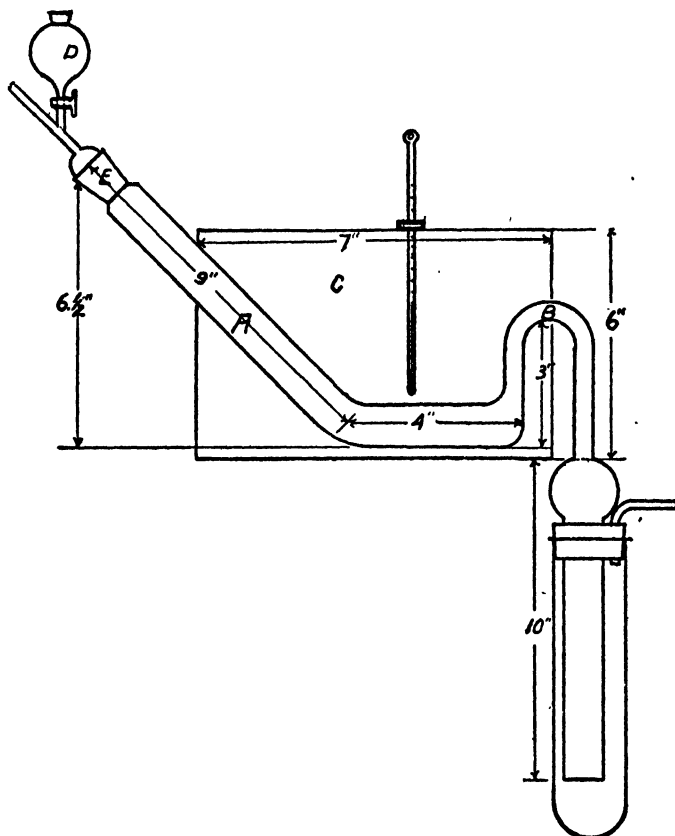
My next thought was to treat an antimonio-tungstate precisely as had been done with the arsenio-tungstate. The following data proved the concordance of results obtained by the method:

Samples.	Percentage $\text{Sb}_2\text{O}_3$ .	Percentage $\text{WO}_3$ .
0.1462 g.	66.87	16.07
0.0799 g.	66.84	16.02
0.1090 g.	66.81	15.96
0.1811 g.	.....	15.90
0.1582 g.	66.85	15.86
0.3040 g.	67.01	16.05

I had the following experience with a sodium vanadio-tungstate: When the dry hydrogen chloride was passed, the vanadium volatilized as a red vapor, condensing to a reddish brown liquid (the oxychloride). The residue was, however, soon reduced to a brownish mass no longer attacked, but on introducing chlorine gas along with the hydrogen chloride the vanadic acid was quite rapidly and completely expelled.<sup>1</sup>

<sup>1</sup> McAdam, *J. Am. Chem. Soc.*, 32, 1603 (1910).

In most satisfactory separations I employed a form of the apparatus pictured in the sketch.



The tube was made in one piece as shown. It consisted of one-inch soft glass tubing, A, to which was sealed a one-half inch exit tube, B. To the exit tube a calcium chloride tube was sealed; this prevented the water from being drawn back into the hot tube. The receiver was a large test tube. A tin box, C, served as an oven. It was provided with a thermometer. By sealing on D, a small separatory funnel, the sample could be moistened without "breaking" the ground-glass joint E. The dimensions should be about as given. Such a piece is easily cleaned, and the vanadium will not diffuse back to the joint. After it is once started it requires no attention.

Chlorine was generated by dropping hydrochloric acid upon potassium permanganate. Hydrogen chloride was generated in the usual manner. The mixed gases were passed through two wash bottles containing sulfuric acid.

In the actual working, weighed portions of the vanadio-tungstate were introduced into the tube by means of a piece of glazed paper. On passing hydrogen chloride, containing a small amount of chlorine, the sample was attacked with the formation of the customary reddish brown volatile liquid. After a time a gentle heat was applied to the oven, and the temperature was gradually increased until it reached  $200^{\circ}$ . A green residue, soluble in water, after evaporation becomes again volatile in hydrogen chloride. If the vanadium condenses in the neck of the tube it should be allowed to distil off slowly in the stream of hot hydrogen chloride.

After about an hour the reduction tube was cooled, and 5 cc. of a 10% sodium hydroxide solution were added.<sup>1</sup> On evaporating in a stream of the gases it was again heated, for one-half hour, at  $200^{\circ}$ . It was then alternately moistened with water and treated with the gas mixture until the red vanadium oxychloride no longer appeared in the cool portion of the exit tube. The rear end of the tube was then rinsed out, a second receiver put in place, and the operation repeated.

The appearance of the red film proved to be a very delicate test for vanadium. When it no longer showed it was always found that the vanadic acid had been completely expelled. The precaution of an extra treatment was, however, observed.

The tungsten was removed from the tube with ammonium hydroxide, and then determined as described under arsenic.

Various methods for estimating the vanadic acid were studied, and it was finally decided that the volumetric method, using potassium permanganate, was best suited to the conditions presented by the hydrogen chloride method.

Experiments were made to prove that there was no loss on evaporating a strong hydrochloric acid solution of vanadium. Such a solution was evaporated, in a retort, the distillate was collected and failed to show the slightest color with hydrogen peroxide.

In the determination of the vanadic acid which had been volatilized, and which it was proposed to estimate with potassium permanganate, I proceeded as follows: The receiver, contents, and exit tube, were rinsed into an evaporating dish, 5 cc. of concentrated sulfuric acid were added, and the solution concentrated, as far as possible, on the water bath. It was then heated, over a low flame, until white fumes of sulfuric acid came off. The contents of the dish were next rinsed into an Erlenmeyer flask, diluted to two hundred cc., heated to boiling, and a stream of sulfur dioxide passed in to completely reduce the vanadium to the vanadyl salt.

<sup>1</sup> This was necessary since the vanadio-tungstic acid contained no sodium or potassium, and, for that reason, a soluble residue resulted on treating with hydrogen chloride.

The boiling was continued and a stream of carbon dioxide was passed to expel the excess of sulfur dioxide, after which the solution was titrated, while still hot, with potassium permanganate, previously standardized with pure vanadium pentoxide, which had been reduced in the same manner.

The following results were obtained:

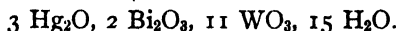
Vanadio-tungstic acid.	Percentage $V_2O_5$ .	Percentage $WO_3$ .
0.2204 g.	.....	65.47
0.3396 g.	.....	65.31
0.3227 g.	16.17	.....
0.3022 g.	15.92	65.35
0.3127 g.	15.90	.....
0.2460 g.	15.95	65.20
0.2487 g.	15.95	65.38
0.1848 g.	16.09	65.39

This method is so satisfactory that I prefer it to the others. The temperature is easily regulated; cooling can be quickly effected by removing the oven; the danger of loss from creeping is slight, and the volatile constituent is more quickly removed.

The methods mentioned above, for the separation of arsenic, antimonie and vanadic acids from tungstic acid seem to me superior to those ordinarily employed, hence I offer them in the hope that they may be of service to others who are called upon to work with similar combinations.

In this connection, I desire to record a further experience with certain "complexes." It will be recalled that Balke and Smith made the potassium, ammonium and strontium salts of a bismuthico-tungstic acid. These salts had the general formula  $3 M'_2O, 2 Bi_2O_3, 11 WO_3 + xH_2O$ .<sup>1</sup>

I prepared the potassium salt and from it obtained the mercurous salt, light yellow in color, well defined and very stable. Its analysis gave the ratio



A portion of this salt was covered with water and hydrochloric acid added in an amount insufficient to decompose the whole of it. After several hours' contact in the cold, with occasional shaking, the residue was filtered out. The aqueous filtrate was evaporated under reduced pressure and at a low temperature. A greenish oil separated when the water was nearly removed. Finally, hydrochloric acid vapors began to appear. Then, the greenish yellow solid was permitted to dry out in a desiccator over solid sodium hydroxide until the odor of hydrogen chloride was no longer perceptible. From an analysis, I at first thought that the hydrogen chloride had taken the place of the water of crystallization; later behavior seemed to indicate, however, that the acid had replaced the mercury oxide, and that the new substance had a composition corresponding to the formula

<sup>1</sup> THIS JOURNAL, 25, 1233 (1903).

6 HCl, 2 Bi<sub>2</sub>O<sub>3</sub>, 11 WO<sub>3</sub>. This is questionable and purely speculative. A new study of the compound is now in progress.

PHILADELPHIA, PA.

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[COMMUNICATION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY OF THE  
UNIVERSITY OF PENNSYLVANIA.]

## NEW DERIVATIVES OF TUNGSTEN.

BY J. BENNETT HILL.

Received September 15, 1916.

As early as 1859, Blomstrand<sup>1</sup> reported a series of compounds of molybdenum derived from the dihalides MoCl<sub>2</sub> and MoBr<sub>2</sub>. These dihalides had been obtained by repeated volatilization of the trihalides in a current of carbon dioxide. The nonvolatile product was soluble in alkalis and from this solution hydrates of the type Mo<sub>3</sub>Cl<sub>4</sub>(OH)<sub>2</sub> were precipitated by weak acids. All of these derivatives were yellow in color. They could be dissolved in strong acids, the nitric acid solutions showing no ionized halogen. The hydrochloric acid solution of the chloromolybdenum hydroxide gave on crystallization, Mo<sub>3</sub>Cl<sub>6</sub>·6H<sub>2</sub>O, and on dilution a pale yellow insoluble compound, Mo<sub>3</sub>Cl<sub>6</sub>·3H<sub>2</sub>O. Mixed halogen derivatives, such as Mo<sub>3</sub>Cl<sub>4</sub>Br<sub>2</sub>·6H<sub>2</sub>O and Mo<sub>3</sub>Br<sub>4</sub>Cl<sub>2</sub>·6H<sub>2</sub>O were also obtained. The chemistry and constitution of these compounds was further developed by Atterberg,<sup>2</sup> Liechti and Kempe,<sup>3</sup> Muthmann and Nagel,<sup>4</sup> Rosenheim and Kohn,<sup>5</sup> and Koppel.<sup>6</sup> Muthmann and Nagel determined the molecular weight of molybdenum dichloride dissolved in ethyl alcohol, and found it to correspond to the triple formula Mo<sub>3</sub>Cl<sub>6</sub>. Rosenheim and Kohn prepared a compound, Mo<sub>3</sub>Cl<sub>6</sub>·HCl·4H<sub>2</sub>O, by dissolving Mo<sub>3</sub>Cl<sub>6</sub> in strong hydrochloric acid, evaporating on a water bath and allowing the solution to crystallize. The compound consisted of glistening yellow needles, soluble in hydrochloric acid but was hydrolyzed by pure water. Only three-sevenths of the chlorine in the compound were ionized.

In 1909, Chapin<sup>7</sup> described halide bases of tantalum. He prepared these compounds by a method previously used by Chabrie<sup>8</sup> for obtaining what he called the dichloride of tantalum. It consisted in heating the pentachloride with 3% sodium amalgam in a hard glass tube sealed at one end and evacuated by means of a suction pump. Chapin used the pentabromide of tantalum. The reaction mass, taken up with water and

<sup>1</sup> *J. prakt. Chem.*, **77**, 88 (1859).

<sup>2</sup> *Jahresb.*, **1872**, 260.

<sup>3</sup> *Ann.*, **169**, 354 (1873).

<sup>4</sup> *Ber.*, **31**, 2009 (1898).

<sup>5</sup> *Z. anorg. Chem.*, **66**, 1 (1910).

<sup>6</sup> *Ibid.*, **77**, 289 (1912).

<sup>7</sup> *THIS JOURNAL*, **32**, 323 (1910).

<sup>8</sup> *Compt. rend.*, **144**, 804 (1907).

hydrobromic acid and evaporated, furnished a crystalline body,  $\text{Ta}_6\text{Br}_{14} \cdot 7\text{H}_2\text{O}$ , dissolving in water to a dark emerald green solution. Chapin further showed that only one-seventh of the bromine in this compound was ionized, indicating the formula  $(\text{Ta}_6\text{Br}_{12})\text{Br}_2 \cdot 7\text{H}_2\text{O}$ . As additional evidence of the correctness of this formula he prepared a number of derivatives of the radical  $\text{Ta}_6\text{Br}_{12}$ , *e. g.*,  $(\text{Ta}_6\text{Br}_{12})\text{Cl}_2 \cdot 7\text{H}_2\text{O}$ ,  $\text{Ta}_6\text{Br}_{12}(\text{OH})_2 \cdot 10\text{H}_2\text{O}$  and others. He determined the molecular weight of the parent bromide in propyl alcohol and found it to correspond to the formula given.

In 1913, Harned<sup>1</sup> reported a similar series of compounds of columbium obtained from the pentachloride by the Chabrie method. He obtained a crystalline body,  $(\text{Cb}_6\text{Cl}_{12})\text{Cl}_2 \cdot 7\text{H}_2\text{O}$ , soluble in water to an olive green solution, a crystalline hydroxide,  $\text{Cb}_6\text{Cl}_{12}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ , and others. Both the columbium and tantalum compounds were characterized by their remarkable tinctorial power, a milligram being sufficient to color 100 cc. of water an intense green.

Harned also obtained a brown compound, insoluble in water, the analysis of which corresponded to the formula  $\text{Cb}_6\text{Cl}_{14} \cdot 9\text{H}_2\text{O}$ . This was prepared by the addition of concentrated hydrochloric acid to the alkaline solution of the green compound  $(\text{Cb}_6\text{Cl}_{12})\text{Cl}_2 \cdot 7\text{H}_2\text{O}$ . The brown derivative, on boiling with water, slowly reverted to the original green. His experiments led him to the conclusion that there was a constitutional difference between the two.

In view of the existence of these compounds of molybdenum, tantalum and columbium, it would seem reasonable to expect that the closely related element, tungsten, would form similar derivatives. Roscoe<sup>2</sup> reported the dichloride, dibromide and diiodide, but a more thorough investigation of them has never been carried out. The present work was undertaken to prepare, if possible, bodies of tungsten similar to those of molybdenum, tantalum and columbium.

To get pure tungsten trioxide from wolframite, the method of purification was that employed by Smith and Exner.<sup>3</sup> The reduction of the pure oxide of tungsten by hydrogen was carried out in a quartz tube, heated to a little over  $1000^\circ$  in a gas-heated furnace constructed of asbestos. The resulting metal with a pale gray color was changed to hexachloride by the process of Smith and Exner and need not be mentioned here. It was found, however, that, while commercial tungsten could be converted to hexachloride at the rate of about 20 g. in two hours, the pure material as obtained above, was only very slowly attacked, seven hours being required to effect the chlorination of 10 g. of metal. Since there was only a trace of oxychlorides formed in the reaction, it was thought that possibly their

<sup>1</sup> THIS JOURNAL, 35, 1078 (1913).

<sup>2</sup> *Ann.*, 162, 360 (1872).

<sup>3</sup> *Chem. News*, 90, 37 (1904).



presence might exert a catalytic action on the chlorination. In an attempt to catalyze the reaction in another way, 0.1 g. of precipitated platinum was sprinkled on the tungsten in the boat. On passing chlorine over the gently heated boat no difference in the speed of the reaction was at first noticed. After a few minutes a glow appeared to run through the mass and, from this point on, the reaction took place as fast as the chlorine could be passed in, the chlorine uniting with the metal with incandescence. By this means 20 g. of tungsten were converted to hexachloride in  $1\frac{1}{2}$  to  $1\frac{3}{4}$  hours. After the tungsten had been swept out, the platinum remained on the bottom of the boat as a brown powder. This was used in the chlorination of the next batch of tungsten and so on repeatedly. Three hundred grams of pure tungsten hexachloride were so obtained.

To reduce the hexachloride in the method outlined by Chabrie and by Chapin, it was mixed in a mortar with a little less than the amount of powdered 3% sodium amalgam calculated to reduce it to the state of dichloride. The mixture was quickly transferred to a Jena tube sealed at one end. The tube, after connecting with a suction pump and evacuating, was gently heated until the reaction had taken place and then heated strongly for about ten minutes. It was allowed to cool in the vacuum, and the contents extracted with hydrochloric acid. On filtering there was obtained a deep reddish brown filtrate and a gray precipitate. Attempts to crystallize the highly colored compound from this solution failed. Its solution was very stable in the air and could be evaporated to dryness with only a trace of decomposition.

Before preparing any quantity of the brown solution the conditions of the reaction were investigated, varying the proportions of the reacting substances and the temperature and duration of heating. As a result the following details were adopted: 15 g. of tungsten hexachloride were ground in a mortar and mixed carefully and quickly with 105 g. of sodium amalgam. The reaction between the two substances is rather vigorous and, unless precautions are taken to prevent it, is liable to take place in the mortar. In view of this, the mortar, as well as both of the reacting substances, were cooled in ice previous to the mixing. In addition to this, not more than ten seconds were allowed to elapse between the time when the amalgam was brought in contact with the hexachloride and the time when the mixture was in the Jena tube with the vacuum on. In spite of these precautions the reaction frequently took place during mixing. When the mixing and transfer to the tube had been successfully accomplished, the reaction was allowed to take place, and the tube then heated just to dull redness and allowed to cool immediately. The contents were extracted with hydrochloric acid (sp. gr. 1.08), and the solution filtered. The brown color so obtained was intense.

A portion of the brown solution was evaporated to dryness and the dry

residue extracted with alcohol. A dark reddish brown solution resulted from which nothing could be crystallized. An extraction with ether gave a yellow solution which on evaporation left a pale yellow amorphous body. This, taken up with a drop of dilute hydrochloric acid and allowed to evaporate, showed under the microscope shining, yellow needles. A somewhat larger portion of the dry residue, treated in a similar way, gave needles as much as a centimeter in length. Experiments with the original brown solution of the reduced mass led to the following method of isolation of the yellow needles: The brown solution was boiled down until considerable sodium chloride had separated out, when it was filtered hot and allowed to cool. There then separated a mixture of sodium chloride and the yellow needles. This was filtered off and washed with concentrated hydrochloric acid until the liquid came through almost colorless. The mixture was spread out on a watch glass and allowed to dry in the air. It was next extracted for about ten minutes under a reflux condenser with ether containing about 5% of ethyl alcohol. The insoluble sodium chloride was filtered out and the ether distilled off from the filtrate, leaving a yellow amorphous mass. This was taken up with fairly strong hydrochloric acid, and boiled when everything dissolved. The clear yellow-colored solution was evaporated to small bulk and allowed to cool, when an abundance of yellow needles separated. These were filtered off, washed with concentrated hydrochloric acid and dried in the air. From 150 g. of tungsten hexachloride, 12 g. of the yellow compound were obtained.

It proved to be readily soluble in alcohol, acetone, glacial acetic acid and in ether containing alcohol, but was almost insoluble in pure anhydrous ether. It was insoluble in benzene, carbon bisulfide, carbon tetrachloride and chloroform. It dissolved in water, but the aqueous solution on standing hydrolyzed, precipitating out first a yellow and then a black compound. The crystals on long exposure to air, or in a desiccator over sulfuric acid, disintegrated, giving a lemon yellow amorphous compound, insoluble in water. The same compound was produced on allowing the solution in dilute hydrochloric acid to stand or on diluting it with water. The resemblance of these two compounds to Rosenheim and Kohn's  $\text{Mo}_2\text{Cl}_6 \cdot \text{HCl} \cdot 4\text{H}_2\text{O}$  and Blomstrand's  $\text{Mo}_2\text{Cl}_6 \cdot 3\text{H}_2\text{O}$  will be at once noticed.

Warm nitric acid effected a complete decomposition of the solution of the yellow needles, a hydrated tungsten trioxide being precipitated in granular form. Potassium hydroxide added to an aqueous solution of the compound gave a clear yellow-colored solution which darkened immediately to a deep brown. From this solution weak acids threw down a black gelatinous precipitate. The same compound was obtained by treating the aqueous solution of the yellow needles with sodium carbonate. The brown alkaline solution on exposure to the air slowly faded in color

to a deep yellow, which with weak acids yielded a yellow gelatinous precipitate.

The determination of tungsten in the yellow needles was obtained by a very simple and direct method. The compound was weighed out in a porcelain crucible, covered with concentrated nitric acid and digested for several hours on a water bath. It was then evaporated to dryness, ignited and weighed as  $\text{WO}_3$ . Results 1 and 2 were obtained by this method; the analyses were made with different preparations of the compound, the results giving evidence both of the accuracy of the method of analysis and of the homogeneity of the product. The third determination was obtained by an altogether different procedure. The aqueous solution of the compound was treated with potassium hydroxide and the deep brown solution acidulated with acetic acid. The black precipitate was filtered off and ignited to trioxide.

No.	Wt. sample.	$\text{WO}_3$ found.	% W.
1.....	0.2223	0.1752	62.50
2.....	0.2271	0.1787	62.42
3.....	0.2009	0.1586	62.62
Average, 62.51%			

The determination of chlorine offered much greater difficulty. It would be fruitless to enumerate the methods attempted. Most of them were valueless for the reason that the silver chloride was contaminated with tungsten. It might be mentioned here that the presence of as little as  $\frac{1}{2}\%$  of tungsten in this precipitate completely alters its character, the silver chloride separating in a granular form rather than curdy. Of the methods attempted the following appeared to be the most satisfactory:

Method 1.—The compound was dissolved in water, treated with ammonia and the solution oxidized with ammonium persulfate. The excess ammonia was boiled off, the tungsten precipitated out as cadmium tungstate and the chlorine determined in the filtrate as silver chloride. Determination 1 was obtained by this method.

Method 2.—The solution of the compound was treated with sodium carbonate and boiled. The black precipitate was filtered out and the silver chloride precipitated in the filtrate. The precipitate showed considerable contamination with tungsten and was dissolved in ammonia and reprecipitated. Determinations 2 and 3 were obtained in this way.

Method 3.—The compound was dissolved in nitric acid (sp. gr. 1.1) and warmed for about two hours when the tungsten completely separated as the hydrated trioxide. This was filtered off and the chlorine determined as silver chloride in the filtrate. The precipitate showed no contamination with tungsten. The results are determinations 4 and 5.

No.	Wt. sample.	AgCl found.	% Cl.
1.....	0.2039	0.2351	28.53
2.....	0.1999	0.2298	28.43
3.....	0.2014	0.2329	28.62
4.....	0.2022	0.2285	27.97
5.....	0.2015	0.2269	27.85
Average, 28.28%			

The water was estimated by the method used by Chapin. The material was mixed with dry lead oxide and heated in a boat in a current of pure dry air to about  $300^{\circ}$  for two hours. The water was collected in a weighed calcium chloride tube. The details of manipulation are those outlined by Chapin.

No.	Wt. sample.	H <sub>2</sub> O found.	% H <sub>2</sub> O.
1.....	0.2007	0.0203	10.11
2.....	0.2008	0.0206	10.26
			Mean, 10.18%

It should be noted that the hydrogen of any hydrochloric acid in the molecule of the compound would appear here as water along with the true water of the compound. The theoretical compositions calculated below are figured on this basis and will, therefore, add up to more than 100%.

It was expected that the composition of the compound would correspond to the formula  $W_3Cl_6.HCl_4.H_2O$ , analogous to Rosenheim and Kohn's  $Mo_3Cl_6.HCl_4.H_2O$ . It will be seen on reference to the figures that the observed values do not agree with those calculated for this substance. They agree much better with the calculated percentages for a compound containing another half molecule of water, the doubled formula of which would be  $W_6Cl_{12}.2HCl_9.H_2O$ . The calculated compositions follow:

Per cent.	Calculated for $W_3Cl_6.HCl_4.H_2O$ .	Calculated for $W_6Cl_{12}.2HCl_9.H_2O$ .	Observed.
W.....	63.20	62.55	62.51
Cl.....	28.46	28.16	28.28
H <sub>2</sub> O.....	9.27	10.20	10.18

The doubled formula finds support in its analogy with the tantalum and columbium compounds. It finds a complete analogy in the columbium compound prepared by Harned and formulated by him,  $Cb_6Cl_{14}.9H_2O$ .

Since the compounds of molybdenum, tantalum and columbium ionize only part of their chlorine in aqueous solution, it seemed reasonable to expect that the yellow tungsten compound would behave similarly. Accordingly an attempt was made to determine the amount of chlorine ionized. In view of the fact that the compound is hydrolyzed in pure water or in dilute acids other than hydrochloric, the problem presented considerable difficulty. The first attempt was to dissolve it in potassium hydroxide solution and to add to the deep brown solution acetic acid, throwing out the black gelatinous precipitate. This was filtered off and the chlorine determined in the filtrate. The operation was conducted entirely in the cold. A similar treatment of the molybdenum compound precipitated a hydrated  $Mo_3Cl_4(OH)_2$  leaving the ionized chlorine in the filtrate. The same behavior was expected here. The following result was obtained:

Wt. sample = 0.2009 | AgCl found = 0.2291 | % Cl = 28.21

This corresponds to the total chlorine in the compound, indicating that a complete decomposition had taken place and that the black precipitate contained no chlorine.

A second attempt was based on the fact, previously mentioned, that the brown alkaline solution on standing fades to a brownish yellow, and that from this solution acetic acid precipitates a yellow-colored substance. A sample of the yellow needles was dissolved in alkali and so treated, the chlorine being determined in the filtrate.

Wt. sample = 0.1017 | AgCl found = 0.1182 | % Cl = 28.76.

The result again indicated a complete decomposition of the needles. It would seem probable that if derivatives in which only a part of the chlorine is split off, are formed at all, they are extremely unstable.

In order to provide further evidence in favor of the formula assigned to the yellow compound, a determination of the molecular weight was sought. An attempt was first made to arrive at this by the lowering of the freezing point of glacial acetic acid. It was discovered, however, that the water of crystallization of the compound interfered to such an extent that no result could be obtained by this method. The rise of the boiling point of ethyl alcohol was next attempted. Here the hydrochloric acid in the molecule appeared to interfere, the boiling point falling on solution of the compound rather than rising. A further investigation along these lines was prevented by lack of material.

### Other Related Compounds.

The lemon-yellow-colored amorphous compound has been described. About a gram of this material was prepared from the yellow needles. It was soluble in boiling hydrochloric acid, reverting to the original yellow derivative. It dissolved in alkalis to give the deep brown solution. Analysis gave the following results:

Wt. sample = 0.2003	WO <sub>3</sub> found = 0.1716	% W = 67.95
Wt. sample = $\begin{cases} 0.2074 \\ 0.2007 \\ 0.1063 \end{cases}$	AgCl found = $\begin{cases} 0.2325 \\ 0.2236 \\ 0.1169 \end{cases}$	% Cl = $\begin{cases} 27.73 \\ 27.57 \\ 27.20 \end{cases}$
Wt. sample = 0.2001	H <sub>2</sub> O found = 0.0107	% H <sub>2</sub> O = 5.35

These values do not correspond to any reasonable formula and it is probable that the compound prepared was impure.

An investigation of the mother liquors from the crystallization of the yellow needles led to the isolation of another compound crystallizing in dark brown shining needles. This was prepared by slowly saturating the mother liquor with hydrochloric acid gas and letting it stand for several days. The sodium chloride thrown out contained, besides yellow needles, a small quantity of the brown compound in crystals about 2 mm. long. The mixture was dried and the brown needles picked out. Only a few

milligrams were obtained. They dissolved in water to a clear yellow-colored solution, not decomposed by boiling nitric acid nor by potassium hydroxide. Sodium carbonate threw out a yellow granular precipitate. The tinctorial power of the compound was remarkable, one of the small crystals giving a decided color to 100 cc. of water. This fact makes it probable that the substance is related to the tantalum and columbium compounds. No analysis was obtained owing to the small amount of substance at hand.

### Investigation of the Alkaline Solution of the Yellow Needles.

It has been mentioned that the addition of alkali to an aqueous solution of the yellow needles produced three distinct solutions: first, a yellow-colored solution which changed immediately to a deep brown, which in turn changed slowly on exposure to the air to a less highly colored brownish yellow solution. It was undertaken here to determine the state of oxidation of the tungsten in these three solutions. The deep brown solution was first investigated. To this end a sample of the yellow compound was dissolved in water and treated with a solution of potassium hydroxide. The solution was let stand for about thirty seconds when it had assumed the dark color. An excess of standard iodine was then added, the color fading to a pale yellow. After standing thirty minutes, the solution was made acid with acetic acid and the excess iodine titrated with thiosulfate. The result is No. 1 in the table. It shows that the tungsten is almost completely in the trivalent condition. The determination was repeated, allowing the alkaline solution to stand ten minutes before the addition of the iodine. The result (2 in the table) shows that the tungsten has been completely oxidized to the trivalent state. Since, from the deep brown solution, weak acids threw out the black gelatinous precipitate which redissolved in alkali to give the original solution, the above results would indicate this black compound to be a hydrated  $W_2O_3$  possibly  $W(OH)_3$ .

The same method was applied to the brownish yellow solution obtained by letting the alkaline solution stand exposed to the air for twenty-four hours. The result (3 in the table) shows that the solution contains quadrivalent tungsten and that the yellow hydrate obtained from it by the action of weak acids must be a hydrated  $WO_2$ .

The first yellow alkaline solution contains tungsten of undoubtedly the same state of oxidation as the yellow needles. The rapidity with which it oxidizes made it rather more difficult to investigate than the other two. To avoid this difficulty the iodine solution was added to the potassium hydroxide and the mixture then added to the water solution of the yellow compound. It was let stand thirty minutes, made acid, and titrated as before. The result is No. 4. It indicates bivalent tungsten, which was, of course, to be expected.

No.	Wt. sample.	I absorbed.	Calc. for W'.	Calc. for W''.	Calc. for W'''.
1.....	0.1007	0.138	0.174	0.131	.....
2.....	0.1008	0.131	0.174	0.131	.....
3.....	0.1016	0.089	.....	0.132	0.088
4.....	0.1009	0.167	0.174	0.131	.....

### Summary.

1. The action of chlorine on tungsten metal to form hexachloride is catalyzed to a remarkable degree by the presence of a small amount of platinum black.

2. Tungsten forms the compound  $W_6Cl_{12} \cdot 2HCl \cdot 9H_2O$ , resembling the molybdenum derivative  $Mo_3Cl_6 \cdot HCl \cdot 4H_2O$ , prepared by Rosenheim and Kohn.

3. The alkaline solution of the preceding compound oxidizes readily and from the solution stable hydrates of trivalent and quadrivalent tungsten were obtained:

PHILADELPHIA, PA.

[CONTRIBUTION FROM THE LABORATORY FOR CHEMISTRY OF FOREST PRODUCTS, UNIVERSITY OF WISCONSIN.]

## THE EFFECT OF PRESSURE UPON THE POTENTIAL OF THE HYDROGEN ELECTRODE.

BY N. EDWARD LOOMIS AND S. F. ACREE.

Received August 28, 1916.

In the previous work by the authors,<sup>1</sup> by Desha,<sup>2</sup> Myers,<sup>3</sup> and by Clarke,<sup>4</sup> it was shown how to make hydrogen and calomel electrodes which can be read to a few millionths of a volt. It was further found that by using a large number of hydrogen and calomel electrodes in batteries to reduce errors, by thoroughly saturating the acid solutions and electrodes with hydrogen before connecting the systems, by using a saturated (4.12 *N*) solution of potassium chloride to annul the contact potential as completely as possible, and by using wide connecting tubes and large fresh contact surfaces, and keeping the barometric pressure constant, it is possible to reproduce readings in a given series to close to 0.00001 volt. Recent investigations of our own and by others<sup>5</sup> have shown that these methods must be adhered to closely for work of the highest precision and accuracy.

The two greatest sources of uncertainty in this work are contact potential and the potential of the hydrogen electrode when incompletely saturated, and, because of these, high reproducibility of readings does not mean corresponding high accuracy. We, therefore, devised,<sup>6</sup> in 1910-11,

<sup>1</sup> *Am. Chem. J.*, 46, 585, 621 (1911); Loomis, *J. Phys. Chem.*, 19, 660 (1915).

<sup>2</sup> *Am. Chem. J.*, 46, 638, 641, 643, 647 (1911).

<sup>3</sup> *Ibid.*, 50, 396 (1913).

<sup>4</sup> *J. Phys. Chem.*, 20, 243 (1916).

<sup>5</sup> Clarke and Lubs, *J. Biol. Chem.*, 25, 479; Ellis, *This Journal*, 38, 737 (1916).

<sup>6</sup> *Am. Chem. J.*, 46, 585, especially Dissertation, J. H. U., p. 29, 609, footnote.

an automatic pressure regulating device involving a Fues normal barometer and electrical equipment for measuring the e. m. f. while keeping the hydrogen at normal and any other desired pressure while it passes through the system. Because of other work, however, we have not yet been able to take up all the problem outlined of studying the effect of hydrogen pressure on the e. m. f. at different temperatures, of measuring the rate of establishment of the gaseous and electrical equilibrium within the electrodes of different materials having different kinds of surfaces in order to study constant and especially *changing* solutions, and especially the problem of studying the mechanism of the establishment of the equilibrium between the molecules, atoms, and ions of hydrogen in and at the different kinds of electrodes. This last phase of the problem is also being studied by Prof. Edward Bennett and one of us in our investigations on the conductivities of solutions. Especial attention will be given to the well-known facts that between 100° and 180° hydrogen dissolves in palladium as hydrogen atoms<sup>1</sup> up to about 400 mm. and above this pressure chiefly as H<sub>2</sub> to the extent of about 900 volumes. Platinum black<sup>2</sup> dissolves about 100 volumes oxygen and 110 volumes of hydrogen up to 300 mm. and above this pressure up to 4.5 atmospheres. The volume absorbed is practically constant for hydrogen but increases 8.5 volumes for oxygen. This last point may be significant in connection with the fact that the hydrogen-oxygen cell gives only 1.08 volts instead of 1.23. Experiments will be performed at 1–3000 mm. at different temperatures to see whether at the critical pressures discussed above, 300 mm. and 400 mm., there is any break in the e. m. f.-pressure-temperature relation should involve (P — 300) and (P — 400) instead of P.<sup>3</sup> This effect of pressure on the electromotive force must be considered all the more important because of such work as that of Harris<sup>4</sup> in which he found that in hydrogen gas the negative charge is associated with 1, 3 and 6 molecules of hydrogen and that the positive charge is associated with 9 molecules of hydrogen. A discussion of all of these relations will be found in another article.

When the work of Loomis and of Myers was carefully considered the data seemed to fit in best with the barometric corrections deduced from the formula  $E = RT/nF \log n \text{ H}_2/\text{H}'_2$ , in which  $n$  was chosen as unity for the balance of the hydrogen ions. But the corrections were so small, and were so masked by such other errors as contact potential that it was shown that the same average values were obtained whether a barometric correction was applied or not. In view of these uncertainties and the fact that no one else had had occasion to work with the precision requiring

<sup>1</sup> Hoitsema, *Z. physik. Chem.*, **17**, 1 (1895).

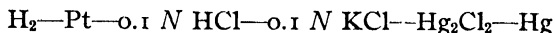
<sup>2</sup> *Ibid.*, **19**, 25 (1896).

<sup>3</sup> *Z. physik. Chem.*, **17**, 1 (1895).

<sup>4</sup> *Phil. Mag.*, **31**, 339 (1916).



the solution of this problem, it seemed desirable<sup>1</sup> to get direct evidence on the effect of wider variations of pressure upon the potential of the hydrogen electrode, especially in the chain



upon which most of the work had been done. The experiments described in this article show that the corrections in the data of Loomis and Myers obtained by the use of the above equation are double the values now found, as has been pointed out by Loomis.<sup>2</sup> When the proper corrections are applied to all our data there are no changes in the general averages because, as pointed out before,<sup>3</sup> the average barometric pressure in Baltimore is practically 760 mm. The same average value 0.4272 is obtained for the data of Myers and Clarke as we obtained in the present study of the electromotive force on the hydrogen electrode in 0.1 *N* hydrochloric acid against calomel in 0.1 *N* KCl.

This work, therefore, shows that the absorbed molecular hydrogen in the electrode is proportional to the  $1/2$  power of the hydrogen pressure or that the absorbed molecular gas gives hydrogen atoms in accordance with the equations  $\text{H}_2 = K \times 2\text{H}$ , and  $\text{H}^+ = K' \times \text{H}$ , either condition leading to the equation  $E = RT/2F \log n p_1/p_2$ , as discussed in another paper. Our work, therefore, harmonizes with that of Czepinski,<sup>4</sup> Haber and Foster,<sup>5</sup> Lewis and Rupert,<sup>6</sup> and of Ellis,<sup>7</sup> who recently made one direct measurement of the effect of pressure on the hydrogen electrode.

The method used in obtaining the results given in this paper was to measure the hydrogen electrode in 0.1 *N* hydrochloric acid against the calomel electrode in 0.1 *N* KCl with no intermediate solution, first at barometric pressure and then at increased or decreased pressure. The arrangement of the solutions was such that increase in pressure caused very slight shifting of the solutions. Contact between the two solutions was made in a wide tube as in all our other work and as recommended since by Cummings and Gilchrist,<sup>8</sup> and by Clarke and Lubs.<sup>9</sup> In order to get constant potentials it was found necessary to renew the surface of contact between the two electrolytes at each set of readings. All measurements were made at 25°.

The apparatus used in making the measurements was the same as

<sup>1</sup> *Am. Chem. J.*, **46**, 585, 609, footnote.

<sup>2</sup> *J. Phys. Chem.*, **19**, 663 (1915).

<sup>3</sup> *Am. Chem. J.*, **46**, 626 (1911), footnote.

<sup>4</sup> *Z. anorg. Chem.*, **30**, 1 (1902).

<sup>5</sup> *Ibid.*, **51**, 289 (1906).

<sup>6</sup> *THIS JOURNAL*, **33**, 299 (1911).

<sup>7</sup> *Ibid.*, **38**, 737 (1916).

<sup>8</sup> *Trans. Faraday Soc.*, **9**, 174 (1913).

<sup>9</sup> *J. Biol. Chem.*, **25**, 491 (1916).

that which has already been described in previous papers from our laboratory.

One experiment is described in detail to illustrate the method in which the measurements were carried out.

8.40 A.M.	E. M. F. experiment started.	8.40 A.M.	E. M. F. experiment started.
9.16	0.42583	Increased pressure to atmospheric + 40 mm.	
9.35	0.42634	10.19	0.42701
9.43	0.42642	10.26	0.42717
9.54	0.42654	10.36	0.42721
9.56	0.42652	10.40	0.42722

Bar. (corrected) = 735 mm.

Pressure = 735 + 40.

Corresponding to an increase in pressure of 40 mm. there is an increase in potential of  $0.42722 - 0.42652 = 0.00070$ .

In calculating the change in potential of the hydrogen electrode from the equation

$$E = \frac{RT}{2F} \log n \frac{p_1}{p_2} = \frac{0.05915}{2} \log_{10} \frac{p_1}{p_2},$$

it has seemed more logical<sup>1</sup> to use for  $p_1$  and  $p_2$  not the total pressures of the system but the partial pressures of the hydrogen, *viz.*, the total pressures minus the vapor pressure of the water solution, practically the same as that of pure water for dilute solutions. There is a difference<sup>2</sup> of only a few hundred thousandths of a volt in the two ways of calculating and our results are not sufficiently accurate to indicate which method of calculation gives the better results.

Applying the equation to this experiment we have

$$E = \frac{0.05915}{2} \log_{10} \frac{775 - 24}{735 - 24} = 0.00070.$$

In this case there is perfect agreement between the measured and theoretical values.

To indicate the steadiness of the electromotive force of the system this same experiment may be followed somewhat further. After the measurement at 775 mm. had been made the pressure upon the system was increased to 789 and then allowed to fall to the original pressure of 735 again. The reading at 789 was 0.42749 at 11.09 A.M. The pressure was released and the subsequent readings were as follows:

Time.....	11.17	11.26	11.34	11.41	11.45	11.48	11.54
E. m. f.....	0.42683	0.42654	0.42647	0.42645	0.42648	0.42651	0.42653

It will be noted that the last two readings are practically identical with those two hours earlier at the same pressure.

The following table summarizes the results which were obtained in eight

<sup>1</sup> Loomis and Acree, *Am. Chem. J.*, **46**, 610 (1911), footnote. Ellis and Clarke and Lubs have now adopted this method.

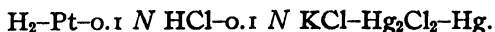
<sup>2</sup> Loomis and Acree, *Am. Chem. J.*, **46**, 610 (1911), footnote.

teen similar experiments. The readings at different time periods are omitted and only the final e. m. fs. obtained at equilibrium are given.

Pressure Change.		Difference of Potential.	
Meas.	Corr. for vapor tens.	Meas.	Calc. ( $RT/2F \log p_1/p_2$ ).
743.5-785.5	719.5-761.5	+0.00099	+0.00073*
740 -778	716 -754	+0.00053	+0.00066*
778 -742	754 -718	-0.00067	-0.00063
742 -788	718 -764	+0.00075	+0.00080
788 -742	764 -718	-0.00076	-0.00080
742 -794	718 -770	+0.00086	+0.00092
739 -760	715 -736	+0.00043	+0.00037
760 -738.5	736 -714.5	-0.00046	-0.00038
733.5-763	709.5-739	+0.00052	+0.00052
735 -775	711 -751	+0.00070	+0.00070
775 -789	751 -765	+0.00027	+0.00024
789 -735	765 -711	-0.00096	-0.00094
735 -785	711 -761	+0.00097	+0.00087*
785 -734.5	761 -710.5	-0.00090	-0.00088
734.5-780.5	710.5-756.5	+0.00078	+0.00081
734.5-809.5	710.5-785.5	+0.00125	+0.00129
735 -794.5	711 -770.5	+0.00119	+0.00103*
794.5-733.5	770.5-709.5	-0.00121	-0.00106*

The first two experiments are to be considered as preliminary ones. The poorer agreement in these is probably due to the fact that fresh surfaces of contact between the two solutions were neglected. The lack of agreement in the fifth from the last is probably due to incomplete saturation or to a change in the potential of the calomel cell, possibly due to shaking, as indicated by the fact that when the pressure was released the electrode failed to come back to its original value by an amount very close to the difference between the theoretical and measured values. In the two final experiments the temperature of the bath varied. But even in these experiments the changes in e. m. f. obtained are much closer to the theory than to double this amount. These experiments marked \* are omitted from the final average. For the remaining determinations the average change in potential per mm. change in pressure is 0.00001751; that calculated is 0.00001746, a variation of 0.29%.

This series of experiments also gave opportunity for further measurements of the potential of the system



The average values of previous measurements of this system by Bjerrum (1) Loomis and Acree (2), and Myers and Acree (3) are 0.4273, 0.4269 and 0.4273, respectively, after correcting for barometric pressure, for the vapor tension of the solution at the hydrogen electrode, and for the present voltage of the Weston cell, and the average is 0.4272. For a more complete summary of these measurements see Loomis and Meacham in an article soon to be published. The following table gives the measured

voltage of five experiments with the above system at 25° with corrections for the potential of the calomel cell, for the barometric pressure, and for the vapor tension of the solution, and the final corrected voltage. The corrections for the potential of the calomel cell were determined as usual in our laboratory by comparing the working electrode with the mean of a large battery containing ten other electrodes. The couplets in the first column give the e. m. f. observed at first under atmospheric conditions and again at this pressure after having subjected the system to the increased pressure.

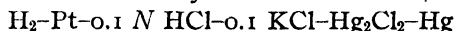
Meas. E. M. F.	Corrections.			Corrected. E. M. F.
	Cal. cell.	Bar. "	Vap. T.	
0.42636	+0.00013	+0.00031	+0.00040	0.42720
0.42635	+0.00013	+0.00031	+0.00040	0.42719
0.42661	—0.00013	+0.00036	+0.00040	0.42724
0.42658	—0.00013	+0.00036	+0.00040	0.42722
0.42652	—0.00009	+0.00042	+0.00040	0.42725
0.42653	—0.00009	+0.00042	+0.00040	0.42726
0.42645	—0.00001	+0.00042	+0.00040	0.42726
0.42609	+0.00035	+0.00039	+0.00040	0.42723

Average, 0.42723

### Conclusions.

1. Experiments on the influence of the partial pressure of hydrogen on the potential of the hydrogen electrode show that near atmospheric pressure the changes can be expressed by the formula  $E = RT/2F \log n H_2/H'_2$ , in which  $H_2$  and  $H'_2$  are the partial pressures. The average change in potential found is 0.00001751 volt per millimeter which is only 0.3% larger than the value 0.00001746 volt calculated by the use of the above formula.

2. Five experiments on the system



gave the potential  $0.42723 \pm 3$ , which is in very close agreement with the average of our earlier values and with those of Bjerrum, namely, 0.4272.

MADISON, WIS.

[CONTRIBUTION FROM THE CHEMISTRY OF FOREST PRODUCTS, UNIVERSITY OF WISCONSIN.]

## STUDIES IN THE MEASUREMENT OF THE ELECTRICAL CONDUCTIVITY OF SOLUTIONS AT DIFFERENT FREQUENCIES.

### V. INVESTIGATIONS ON THE USE OF THE VREELAND OSCILLATOR AND OTHER SOURCES OF CURRENT FOR CONDUCTIVITY MEASUREMENTS.<sup>1</sup>

BY W. A. TAYLOR AND S. F. ACREE.

Received August 26, 1916.

As the measurement of the true electrical conductivities of solutions

<sup>1</sup> Robertson and Acree, *J. Phys. Chem.*, **19**, 381 (1915); Taylor and Curtis, *Phys. Rev.*, **6**, 61 (1915); Taylor, *Science*, **42**, 388 (1915). We are indebted to the Carnegie Institution of Washington for aid in this work.

of electrolytes and of heterogeneous systems, such as woods and other plant tissues and their liquid contents, skin and muscular tissues under different conditions, blood and many colloidal solutions and suspensions is of great importance to chemists, physicists, botanists, zoölogists, geologists, medical men, and others, we have been working during the past few years to develop methods for this purpose with an accuracy of 0.001%. The most important new aspects of the investigation were to determine the nature of the electrode processes, the polarization or capacity phenomena, and the phase relations, by the use of pure resistances, capacities, inductances, the oscillograph and an alternating current potentiometer. Since the ideal condition of being able to measure the true resistance at high frequencies approaching infinity cannot be realized today because of errors from skin effects and inductance and capacity in the resistance coils and leads, and because there are no current detectors giving the necessary precision at such high frequencies, we have tried to find methods for using lower frequencies. In this work it was first necessary to obtain a source of alternating current which has a pure sine wave form of any desired voltage and of constant frequency, which frequency may be varied at will through a wide range. A pure sine wave is required in order to prevent unsymmetrical polarization at the electrodes and to annul the influence of harmonics on the telephone; that is, to obtain complete silence when the fundamental frequency is perfectly balanced by the use of the correct resistance and inductance or capacity in the bridge. Since we have found that the apparent resistance of a given solution in a cell with bright electrodes may vary as much as several per cent. with change in frequency, and that the true electrical resistance can be obtained only by making resistance measurements at several different frequencies and extrapolating the resistance to infinite frequency, or applying the formula  $R_{\infty} = R_f - KL_{ff}$ , it is obvious that we must be able to change the frequency at will, but that it must be constant at any given setting.

In our work we have tested the induction coil,<sup>1</sup> the 60-cycle city current of Madison, a Holzer-Cabot wireless alternating current generator, a General Electric type of large generator, a Siemen's-Halske alternating current generator, the small Vreeland oscillator sold by Leeds & Northrup for work at 500 and 1000 cycles, and the very fine type<sup>2</sup> B Vreeland oscillator which the Western Electric Company sells for work at frequencies varying from 160 to 4200 cycles. Oscillograms of the wave forms of the different machines are given in the figures below. These photographs show the wave form of the voltage, and also that of the current in some

<sup>1</sup> See Leeds and Northrup Catalogue 48, for oscillograms of their induction coils and of their small Vreeland oscillator, and for a description of this latter instrument.

<sup>2</sup> See "The Vreeland Oscillator" issued by the Western Electric Co., for a description of their Vreeland Oscillators, the oscillograms, and general applications of these instruments.

cases. In the case of the Madison city current the wave form of the charging current of a condenser supplied with this voltage is also shown to give an idea of the harmonics present. The writers are greatly indebted to Messrs. Curtis, Fitch and Fearing of the Bureau of Standards and to Professor Edward Bennett and Dr. G. H. Gray of the University of Wisconsin, for assistance in obtaining these oscillograms at various times since 1911.

The induction coil should be discarded when conductivity measurements of any great degree of accuracy are desired. It is especially unfitted for this work because (1) it does not give an alternating but a pulsating current having a large number of over-tones which prevent the operator from obtaining complete silence in the telephone, (2) the range of frequency is comparatively small, and (3) it is impossible to keep the frequency constant. Figs. I and II show the voltage wave form given by our induction coil, which is one of the best types made by Leeds and Northrup. This wave form is not only clearly far from sinusoidal, but is very unsymmetrical. The electromotive force below the axis is considerably larger than that above and the much slower rise to the maximum above is in decided contrast to the sharp break into the axis from below. The unreliability of an induction coil is clearly shown by the fact that although Figs. I and II were made without changing the setting of the induction coil, the difference between the amplitudes of the upper and lower peaks in Fig. I is much larger than in Fig. II. These facts show clearly not only that there is unsymmetrical polarization at the electrodes but that it varies so much from moment to moment when an induction coil is used that it is impossible to have the same current or voltage phases at the telephone terminals and secure silence.

Fig. III gives the oscillogram of the voltage wave of the 60-cycle city current of Madison. It is seen that the wave form is nearly sinusoidal, although the irregularities at the crest of the wave show that some harmonics are present. Fig. IV shows the oscillogram of the charging current of a condenser supplied by this voltage. In the charging current of a condenser the amplitude of any  $n$ th harmonic is  $n$  times as great as in the voltage wave form. Fig. V shows the pure sine charging current of the condenser after these harmonics have been tuned out by the use of the proper inductance and capacity. By tuning out the harmonics a very much better and more accurate minimum can be obtained. In Figs. IV and V,  $e$  denotes the voltage and  $i$  the current curves. Although the frequency is not quite steady a very good bridge balance can be obtained for such low frequencies and this purified source of current was useful in getting resistance, capacity and inductance measurements to compare with those at higher frequencies.

Figs. VI and VII give the oscillograms of a Holzer-Cabot wireless gen-

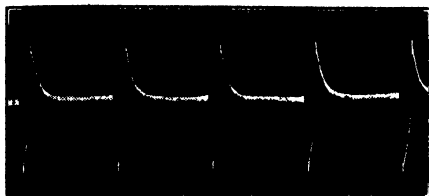


Fig. I.

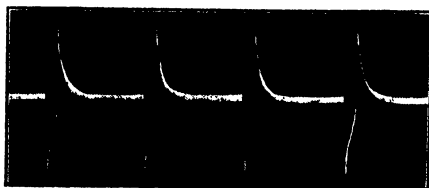


Fig. II.

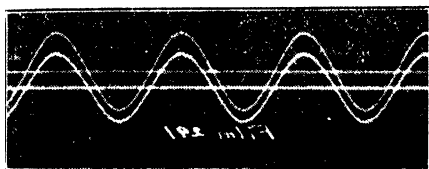


Fig. III.

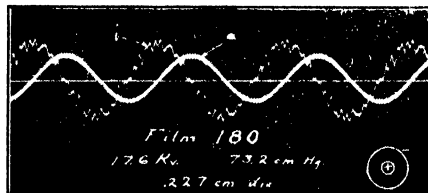


Fig. IV.

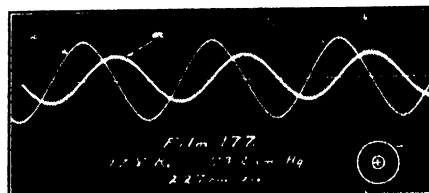


Fig. V.

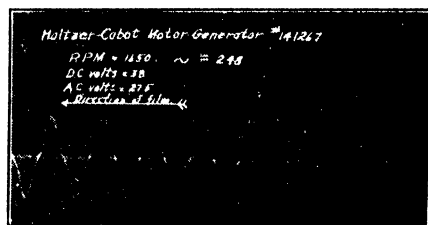


Fig. VI.

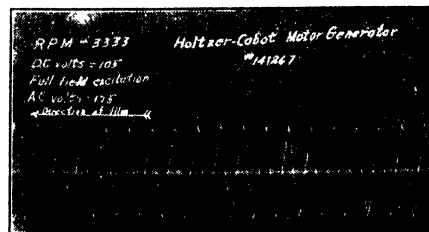


Fig. VII.

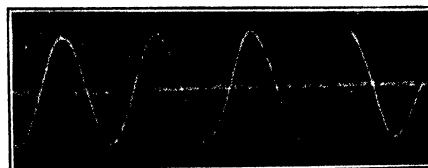


Fig. VIII.

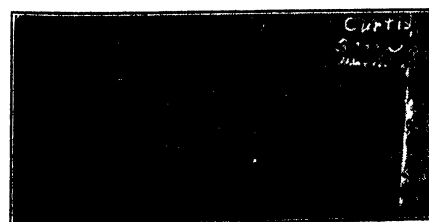


Fig. IX.

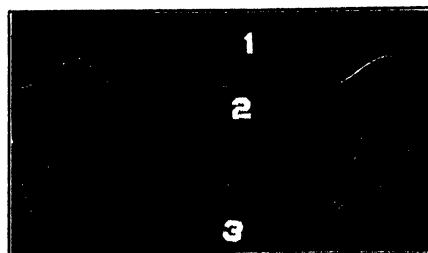


Fig. X.

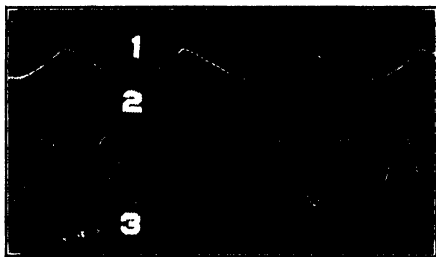


Fig. XI.

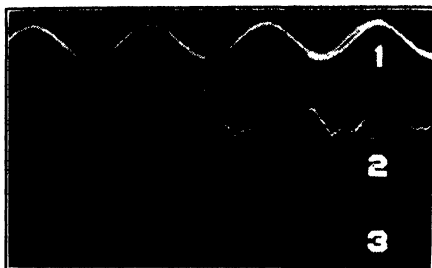


Fig. XII.

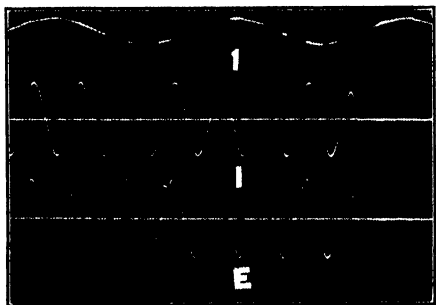


Fig. XIII.

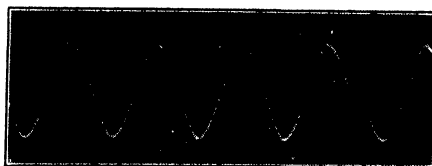


Fig. XIV.



Fig. XV.

erator at 248 and 500 cycles, respectively. Although the wave form is very good for a machine of this kind, it is somewhat flat-topped because of the presence of a third harmonic. This prevents complete silence in the telephone when the fundamental is balanced. The greatest disadvantage is that the machine has no attachment for changing or regulating the frequency.

Figs. VIII and IX give the oscillograms of the wave forms obtained from the large General Electric Company generator made for frequencies from 160 to 3000. The first is for the 600-cycle side of the machine and the second for the 3000 side. These are practically sine waves and the freedom from harmonics allows us to obtain a much better minimum than that given by the Holzer-Cabot machine. But the frequency is not absolutely constant and the cost of the machine is very large. The energy output of the machine is so large that an alternating current galvanometer can be used as current detector at low frequencies with high precision.

Curtis in his work on resistances for alternating currents, and Washburn in his fine work on conductivities, and also Schlesinger have already



tested the Siemens-Halske generator and found it excellent. The harmonics can be easily tuned out by the use of inductances and capacities. It can be made to give frequencies from 400 to 1800 but these are not constant unless a special regulating device is attached.

We have found the type B Vreeland oscillator sold by the Western Electric Company to be far the best source of current tried thus far, for the following reasons: (1) It is practically noiseless and can be started and stopped conveniently. (2) By the use of suitable secondary coils, which can be rotated easily, it can be made to give any voltage desired up to about 500; only a very small current can be obtained at this voltage but this is ample for measuring resistances up to 100,000 ohms or more. When a storage battery of constant voltage is used as a source of actuating current the alternating current obtained has a voltage steady enough for alternating current potentiometry. (3) It gives a constant frequency independent of variations in the actuating direct current or in the load and, hence, under even only fairly constant conditions, gives a note of constant pitch and loudness in the telephone, and, of especial importance, allows the cell capacity to be balanced out sharply so that an accurate bridge balance can be obtained. (4) The frequency is regulated by means of a set of mica and paper condensers with a range of 0.001 to 40 microfarads and in this way can be changed easily to any value between 160 and 4200 cycles and kept constant for weeks to within 0.10%. By changing the number of turns in the field coils of the Vreeland oscillator the frequency can be made as low as 30 to 40 without the use of additional condensers. By using extra condensers or inductances and these special field coils the frequency can be lowered to possibly 10; although Vreeland states that the wave form is not perfect at this frequency it is nevertheless good enough for all of our requirements. By the use of quartz bulbs frequencies up to 100,000 for wireless telegraphy can be obtained. An instrument for giving simultaneously any two frequencies within these ranges is much needed and may later be placed on the market. (5) It gives practically a pure sine wave free from harmonics which disturb the operator using the telephone and, hence, it is possible to obtain easily complete silence in the telephone. (6) It can be run by a mercury rectifier, but the wave form is then not so good, because the rectifier voltage is pulsating and not steady. Our unloaded rectifier gives the pulsating voltage wave form 2 in Fig. X, 1 being the zero of voltage in both Figs. X and XI. When loaded with the Vreeland the rectifier gives the voltage wave form 2 in Fig. XI, and the Vreeland gives the voltage wave form 3. This wave form 3 is seen to have a smaller amplitude every second cycle. The Vreeland gives a fine sine wave when run by the current from a good dynamo, especially if any small irregularity, such as that due to the dynamo brushes, is suppressed, and Fig. XII illustrates a study of their dynamo

by Professor Bennett and Dr. Gray. Line 1 is the voltage oscillogram of the Madison 60-cycle city current and is used for reference. Line 2 shows the harmonics in the voltage wave form from the dynamo, and the entire film shows that the harmonics are repeated every six cycles. It was obtained by passing 3.5 amperes through the primary circuit of a 5 : 1 transformer and taking the voltage oscillogram of the secondary circuit. As the oscillograph was set so that the zero of voltage was 12 feet away and the transformer magnified the harmonics 5 times it is seen that the variation of about 1 inch in the oscillogram corresponds to a change of about  $1/750$  in the voltage from this cause. These harmonics can be suppressed by the use of a proper set-up of inductances and capacities. Line 3 illustrates the improvement secured by using an inductance of 1 henry in series with the primary of a second transformer set-up duplicating in every respect the one described above. As lines 1, 2 and 3 were taken simultaneously it is seen that this inductance chokes out the harmonics so nearly completely that there is no doubt that the current from any dynamo could be purified by using inductance and capacity, and hence the inductance and capacity in the Vreeland automatically tend to purify the dynamo current. When 3.5 amperes from a storage battery were passed through the transformer a perfectly straight voltage line, not illustrated, was obtained. The advantage of using such a purified current from a dynamo over that from a storage battery is simply one of less expense and avoidance of the labor of attending to storage batteries. The voltage, however, is not very constant in even the best dynamo. But a storage battery gives the steadiest current and hence the best wave form from the Vreeland, illustrated in 3, Fig. X, and should be used when convenient. Although the usual Type B instrument is made to operate on direct currents of 110 down to 75 volts, an instrument like ours can be ordered to operate from 120 down to 50 volts and thus effect distinct economy when storage cells are used. (7) In order to regulate the frequency we use calibrated tuning forks of 100, 250, 500, 750, 1000, 1500, 2000 and 3000 vibrations, and by changing the capacity the frequency can be fixed by the "beat" method with an accuracy of 0.10% for the lower frequencies and much better for the higher ones. Having calibrated the Vreeland at several frequencies, it is a simple matter to calculate the capacity necessary for any frequency. As such a set of tuning forks is expensive we shall be glad to lend them to anyone. (8) It is thus seen that no other available instrument so nearly meets ideal conditions for alternating current work in physics and chemistry and no investigator who has once used the Vreeland oscillator will be content with anything less satisfactory. Fig. XIII gives the practically pure sine voltage and current wave forms,  $e$  and  $i$ , for 240 cycles from the Type B Vreeland, when the current is passed through a conductivity cell;

a small third harmonic is present and has been studied by H. P. Hastings.

At the suggestion of one of us, Leeds and Northrup arranged with Vreeland to develop a smaller and less expensive instrument giving 500 and 1000 cycles, which they are now selling. After we had tested the first of these and the development of our work had shown the desirability of certain modifications, especially a wider range of frequency, Vreeland consented to the sale of an instrument giving 500, 750, 1000 and 1500 cycles, which are ample for most work on the simple measurement of the conductivities of solutions. Fig. XIV gives the oscillogram of the wave form of the small Vreeland oscillator at 130 cycles. It should be emphasized that this Vreeland was built by Leeds and Northrup to give frequencies of 500 and 1000 and that we had to add extra capacity in order to get the lower frequency. Even under these extreme conditions the wave form for this lower frequency is still very good. The wave form for 500 cycles in Fig. XV is practically a pure sine wave and gives excellent results in conductivity work.

After making the above study on the best source of alternating current for this conductivity work practically all of our measurements have been made with the Type B Vreeland oscillator. The development of the best types of bridges, telephones, inductances, capacities, cells, baths, etc., and the applicability of various types of bridge set-ups in this work will be described in the succeeding articles. Especially will it be shown that the apparent resistance changes with frequency when bright electrodes are used but that by the proper methods and calculations the true electrical conductivity can be obtained.

MADISON, WIS.

## STUDIES IN THE MEASUREMENT OF THE ELECTRICAL CONDUCTIVITY OF SOLUTIONS AT DIFFERENT FREQUENCIES.

### VI. INVESTIGATIONS ON BRIDGE METHODS, RESISTANCES, CELLS, CAPACITIES, INDUCTANCES, PHASE RELATIONS, PRECISION OF MEASUREMENTS, AND A COMPARISON OF THE RESISTANCES OBTAINED BY THE USE OF INDUCTANCE AND CAPACITY BRIDGES.<sup>1</sup>

BY W. A. TAYLOR AND S. F. ACREE.

Received August 28, 1916.

During the last few years, chemists have made decided improvements in the Kohlrausch method of measuring the electrical conductivities of solutions.

<sup>1</sup> We are indebted to the Carnegie Institution of Washington for aid in this work.

A. A. Noyes<sup>1</sup> and his co-workers made great strides by using weighed solutions and fine bomb-cells, and their work probably has an accuracy of 0.10%.

Washburn<sup>2</sup> published the first fine article on a general improvement of the Kohlrausch method in which he described notable advances by the use of tuned telephones, pure resistances, better cells, a 1000 cycle current of sine wave form, better capacities for securing a minimum, and methods of grounding.

Chapman and Hibbard<sup>3</sup> have recently published an excellent bulletin in which they describe similar apparatus and especially the use of an alternating current galvanometer as a detector for the 60-cycle current obtained from a Holtzer-Cabot generator.

Hartley and Barrett<sup>4</sup> showed an apparent change of resistance with change in frequency, and Schlesinger<sup>5</sup> has described some noteworthy improvements.

The general methods here described had their origin in 1908-9 in the repeated observations that the resistance of solutions apparently changed with a change in the frequency of the current from the induction coil. As this source of error was seen to be a possible explanation of the discrepancies in the results obtained by different investigators using different frequencies and different cells it was decided to investigate as deeply as possible the frequency, resistance and capacity relations. Washburn and Chapman and Hibbard used 1000 and 60 cycles, respectively, and considered that the resistances observed are the true electrical resistances, but our work shows the necessity for measurements at different frequencies, if we are to understand clearly all the phenomena involved in the solution and at the electrodes, and to measure the true electrical conductivities. By deliberately magnifying the different sources of error we have been able to understand them and develop methods for their elimination.

In this study we have been greatly aided by Dr. H. L. Curtis of the National Bureau of Standards, and especially by Prof. Edward Bennett, of the University of Wisconsin, and by other colleagues who have made many important suggestions on the interpretation of our results and on the methods, which are well known to electrical engineers and physicists, but not to chemists in general. Most of the data here reported were worked out by Taylor in Washington with the excellent equipment kindly placed at our disposal by the Bureau of Standards.

In this research the writers have tried (1) to solve the ordinary mechan-

<sup>1</sup> Noyes, Carnegie Inst. Monograph.

<sup>2</sup> Washburn and Bell, *THIS JOURNAL*, 35, 177 (1913).

<sup>3</sup> Hibbard and Chapman, Mich. Agr. Coll., Expt. Sta., *Tech. Bull.* 23.

<sup>4</sup> Hartley and Barrett, *THIS JOURNAL*, 103, 786 (1913).

<sup>5</sup> Schlesinger, *Ibid.*, 36, 1589 (1914).

ical and electrical difficulties connected with the measurement of the conductivity of electrolytes, (2) to make a fundamental study of the *electrode phenomena* and their bearing on the resistance and capacity of a solution in a conductivity cell at different frequencies and voltages, and (3) to eliminate the importance of these electrode phenomena as far as possible so as to make the *apparent* resistance of a solution in a cell as nearly as possible only the *true electrical resistance* of the solution.

**Source of Current.**—The first requisite for securing a bridge balance when resistances, inductances, and capacities are measured, is a source of alternating current which has a pure sine wave form of any desired voltage, and of constant frequency, which frequency may be varied at will through a wide range. This is necessary to prevent unsymmetrical polarization at the electrodes and to annul the influence of harmonics on the telephone, and to enable us to study the effects of changes in voltage and frequency on the resistances of solutions in the cells. After testing the ordinary "buzzer," the Holtzer-Cabot and General Electric generators and the 60-cycle current of Madison, we have found that the Type A or B Vreeland oscillator sold by the Western Electric Company best suited our requirements for many reasons previously published. We are making measurements at 250 to 3000 cycles per second. Arrangements have now been made with Dr. Vreeland, however, for Leeds and Northrup to sell a small instrument for use at 500, 750, 1000 and 1500 cycles, which are sufficient for most work. We use calibrated tuning forks and the beat method to secure the correct frequency.

**Resistances.**—In order to make measurements with a precision or accuracy of 0.001% with alternating currents, the resistances must be so made as to be free from errors from inductance and capacity at all frequencies used. Curtis<sup>1</sup> has shown that average American and German resistances of 1000 ohms and over, including our own Chapeyron coils, may have errors greater than 0.05% arising from inductance and capacity effects, and has devised coils which are practically free from these defects. These coils have been used in our work. These have been used recently by Washburn and by Chapman and Hibbard. Washburn formerly used platinum strips on glass rods devised by physicists and we are indebted to Professor H. Pfundt for the use of one of his type of platinum film on glass plates. It seems to the writers that the great objection to platinum films on glass or quartz is the high temperature coefficient, the fragility, and the inconvenience in mounting or inclosing them.

**Telephones.**—We have used telephones made by the Western Electric Company which are very sensitive and which can be tuned to the particular frequency of the alternating current employed, in order to get the

<sup>1</sup> Curtis and Grover, *Bull. Bur. Standards*, Vol. 8, No. 3 (1911).

greatest accuracy in bridge settings. The attachment of a stethoscope to the telephone, suggested by Curtis, has been a very great aid. We have also used an alternating current galvanometer at low frequencies.

**Bridge.**—Two well-known types of the Wheatstone bridge were recommended to us by Leeds and Northrup, Curtis, and Bennett, and Mr. H. P. Hastings has begun the use of several others. We have employed throughout the work the substitution method used regularly in the Bureau of Standards and suggested to us by Dr. Curtis, and have compared it with others. The arrangement of the bridges is shown in Figs. I and II, and

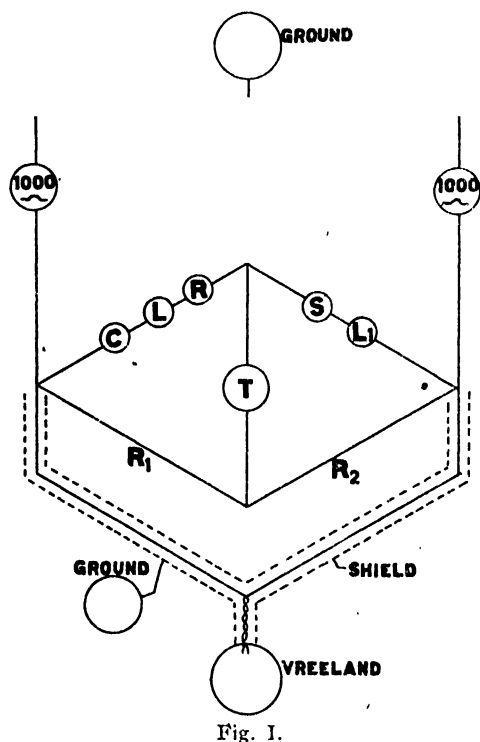


Fig. I.

the substitution method used is explained below.  $R_1$  and  $R_2$  are Curtis ratio coils of 100, 500, or 1000 ohms each,  $C$  the cell,  $T$  the telephone,  $S$  the variable resistance in the bridge,  $L$  a variable standard inductance,  $L_1$  a fixed inductance greater than the smallest value of  $L$ ,  $K$  a standard variable condenser,  $K_1$  a variable or fixed condenser with a capacity larger than the lowest value of  $K$  if the bridge cannot be balanced by  $K$ , and  $R$  a set of fine variable Curtis resistances with a range from 10,000 to 0.001 ohm. In making a reading with the bridge shown in Fig. I,  $R$  is set on zero, and, with the cell in circuit,  $S$  and  $L$  are varied until there is no sound in the telephone. The cell is then removed and the bridge again balanced by varying  $L$  and  $R$ . The reading of  $R$  is then the sum of the "apparent" resistances of the cell and of the cell leads and electrodes, whose resistances are known, and the difference between the two inductance readings gives the inductance corresponding to the cell "capacity." It is then necessary simply to regulate the temperature of  $R$  and by this method we eliminate any error due to changes in the other resistances, or in the inductances, arising from changes in room temperature. With good temperature regulation measurements on a cell can be duplicated to one part in 100,000. In making a reading with the bridge shown in Fig. II a similar procedure should be employed, *i. e.*, the bridge is first balanced with the cell and the

the substitution method used is explained below.  $R_1$  and  $R_2$  are Curtis ratio coils of 100, 500, or 1000 ohms each,  $C$  the cell,  $T$  the telephone,  $S$  the variable resistance in the bridge,  $L$  a variable standard inductance,  $L_1$  a fixed inductance greater than the smallest value of  $L$ ,  $K$  a standard variable condenser,  $K_1$  a variable or fixed condenser with a capacity larger than the lowest value of  $K$  if the bridge cannot be balanced by  $K$ , and  $R$  a set of fine variable Curtis resistances with a range from 10,000 to 0.001 ohm. In making a reading with the bridge shown in Fig. I,  $R$  is set on zero, and, with the cell in circuit,  $S$  and  $L$  are varied until there is no sound in the telephone. The cell is then removed and the bridge again balanced by varying

condensers  $K$  and  $K_1$  in circuit. Then the cell is removed and the bridge again balanced by changing  $R$  and  $K$ . The resistance and capacity of the cell are then obtained as above.

The method of grounding the bridge was developed by Curtis and Taylor and other methods and improvements will be described later by Mr. H. P. Hastings.

This bridge set-up in Fig. II, with the exception of the substitution method and the grounding, is the one devised by Kohlrausch and improved with great success first by Washburn and Bell<sup>1</sup> and later by Hibbard and Chapman. These workers, however, did not use Curtis ratio coils but employed the circular Kohlrausch slide wire bridge. It will be shown in a subsequent article that even a mechanically perfect circular Kohlrausch slide wire bridge must be used with very great caution as errors as large as 1% can arise in some bridge set-ups because of the self-induction in the circular slide wire and the capacity between the metal cover and the slide wire.

We have now devised and used extensively a special bridge containing Curtis ratio and dial coils and inclosed Curtis alternating current standards similar to the National Bureau of Standards' fixed resistances for direct currents. These are all immersed in oil at constant temperature and the resistances can be relied upon very accurately. They are furthermore calibrated by direct current against a set of four National Bureau of Standards resistances of the inclosed type. This apparatus was built for us by Leeds and Northrup and it will be described and the measurements reported in the near future in other articles.

**Capacities.**—Our condensers consist of (1) a Western Electric Company box of standard mica units from 0.001 to 1.1 microfarads and paper units up to 41.1 microfarads and (2) a Leeds and Northrup variable air condenser, giving from  $25 \times 10^{-6}$  to  $1500 \times 10^{-6}$  microfarads. We have

<sup>1</sup> THIS JOURNAL, 35, 197 (1913) and Catalog No. 48 of Leeds and Northrup (1915).

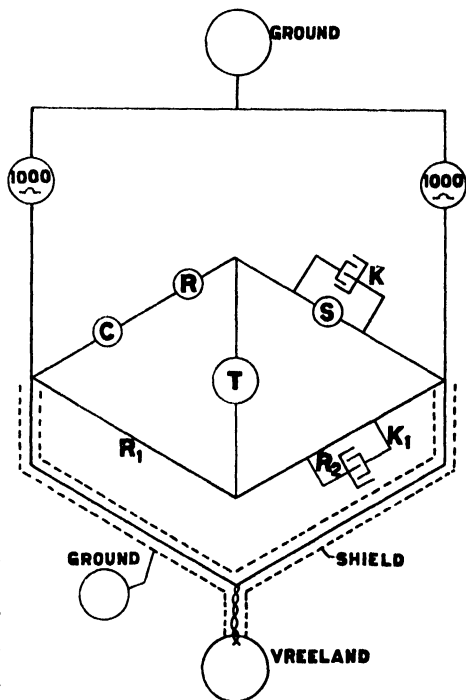


Fig. II.

also three other variable air condensers of low range. These standards have either been calibrated by the Bureau of Standards or checked by us against our standards. These measurements were, of course, made at the different frequencies used by us.

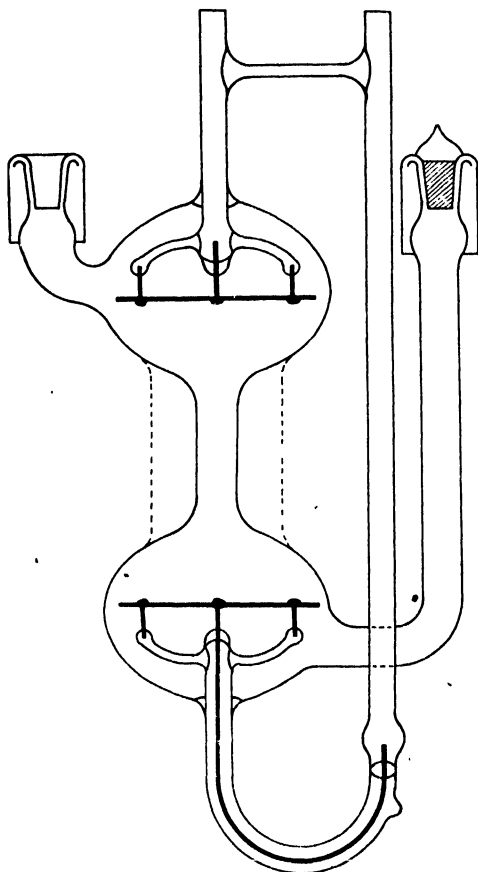


Fig. III.

**Inductances.**—Our fixed inductances are wound in a single layer on mahogany spools, as we have found that multiple layers produce changes in resistance and inductance when the frequency is changed. Stranded and braided enameled silk covered wire should be used at high frequencies to prevent errors from "skin effects." Our variable inductances are improved forms of the Ayrton and Perry types on mahogany frames worked out in cooperation with Professor Edward Bennett and are so devised as to be practically free from changes in resistance and inductance arising from changes in frequency. They are arranged with verniers and mechanical devices which allow us to obtain quickly and accurately values from  $10^{-3}$  millihenries upward. They will be

described in detail in separate articles.

**Phase Relations.**—The resistance of a solution in a conductivity cell is made up of the *true resistance* of the solution and certain phenomena which we shall call *electrode effects*. A cell behaves toward an alternating current as if it were made up of a resistance in series with a condenser with a small leak, and it offers an impedance to the harmonically varying current, changes the phase in that bridge arm, and gives an unbalance in the telephone. It is, therefore, impossible to obtain a perfectly sharp minimum in the telephone unless the capacity is accurately balanced by one of the several well-known methods, such as (1) a capacity in parallel with the resistance arm of the bridge, as recommended by Kohlrausch, (2) a capacity in series with the resistance arm of the bridge, (3) an in-



ductance in series with the cell (in R, Fig. I), or (4) an inductance in the opposite side of the bridge (in R<sub>2</sub>, Fig. I). We have used all of these methods and have compared them with others and our results will be given in a later report.

Mr. H. P. Hastings has observed the very interesting and fundamentally important phenomenon that in cells with small bright electrodes a disturbing third harmonic accompanies the low fundamental note from the Vreeland oscillator at low frequencies, and this has also been observed in oscillograph measurements by Dr. G. H. Gray. This harmonic can, of course, be balanced out by an inductance or capacity, and its frequency can be thus calculated. We have devised methods for balancing out the fundamental notes, and the harmonics simultaneously, in order to study the electrode phenomena more carefully. A Vreeland oscillator giving simultaneously two or more frequencies of any desired values is greatly to be desired.

**Cells.**—Our cells are dumb-bell types which we have developed since 1908 and are shown in Figs. III and IV. They are made by Otto Haak, 545 N. 5th Street, Philadelphia. The advantages of these cells are the following: (1) The ground glass joints are not exposed but are under the

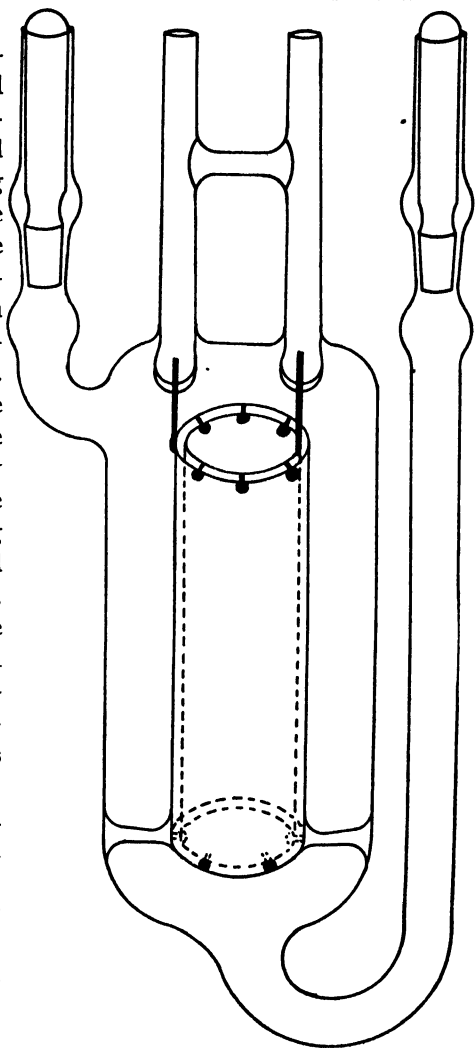


Fig. IV.

liquid of the bath and hence prevent evaporation of the solvent and consequent changes of concentration. (2) The electrodes are supported in four places so that they cannot change position and thus change the cell constant. They can be made of Jena 16<sup>III</sup> or 297<sup>III</sup> glass or of quartz. Our criterion of excellent cells is that *whatever the solutions used the ratios of the resistances of any solution in two such cells, or of two solutions in any*

cell, must be constant to within 0.01% at infinite frequency. Only in this way can we be certain that the electrode effects have been practically eliminated and that we are measuring the *true electrical resistance* of the solution with great accuracy. This we have now succeeded in attaining.

**Solutions.**—The solutions should be made up and analyzed by weight methods in resistance glass or quartz containers and transferred by means of apparatus which will be described in a later report, *under the water* of the constant temperature bath into *clean cells* containing air in which the vapor pressure is that of the solution to be measured. In the present work the solutions were not made up with any great degree of accuracy as we were concerned first with developing accurate *methods* for making conductivity measurements and this problem could be solved as well by relative as by absolute measurements of conductivity.

**Precision of Resistance Measurements on Solutions.**—Using the apparatus described and the method outlined above it will be seen from the TABLE I.—DATA SHOWING PRECISION OF RESISTANCE READINGS ON A GIVEN SOLUTION IN A GIVEN CELL.

Cell V— $\frac{1}{2}$ -inch platinized electrodes.

0.2 N NaCl.	
Time.	Res. at 1000
3.25.....	...
3.38.....	89.142
3.41.....	89.143
3.43.....	89.143
3.45.....	89.143
3.48.....	89.143
3.51.....	89.142
4.12.....	89.143
Next day	
9.31.....	89.143
9.35.....	89.144
Maximum difference, 0.0022%.	

Cell II—1-inch silver plated electrodes.

0.1 N NaCl.	
Time.	Res. at 1000.
3.25.....	...
3.46.....	163.573
3.49.....	163.574
3.51.....	163.573
4.05.....	163.573
4.09.....	163.573
Maximum difference, 0.0006%.	

Cell II—1-inch bright electrodes.

0.05 N NaCl.	
Time.	Res. at 1000
1.45.....	...
2.14.....	313.474
2.17.....	313.474
2.19.....	313.472
2.22.....	313.471
2.24.....	313.470
2.27.....	313.470
2.45.....	313.472
2.57.....	313.471

Maximum difference, 0.0013%.

Cell IX—2-inch sand-blasted electrodes.

0.2 N NaCl.	
Time.	Res. at 1000.
9.35.....	...
10.12.....	282.090
10.14.....	282.092
10.15.....	282.091
10.48.....	282.092
10.51.....	282.094
10.53.....	282.095
10.55.....	282.095
11.04.....	282.092
11.07.....	282.093
11.33.....	282.091
11.35.....	282.091
11.40.....	282.090
Maximum difference, 0.0018%.	

data given in Table I that readings on a given cell with a given solution can be repeated easily with an average deviation within  $\pm 0.001\%$ .

**Checks on the Resistance of Different Parts of the Same Solution in the Same Cell.**—Resistance measurements were then made on different parts of the same solution in the same cell to see how closely these measurements would check. The following table shows that the maximum variation is about  $0.01\%$ . Each measurement given is the average of a large number of readings for the same portion of the solution. Considering the fact that the electrodes in most of the older cells made in 1908 were not absolutely rigid, that the solutions were poured into the cells, etc., these values check remarkably well.

TABLE II.—CHECKS ON DIFFERENT PARTS OF THE SAME SOLUTION IN THE SAME CELL.

	Res. at 1000.	Max. dif. in per cent.
Cell I—1-inch bright electrodes, 0.05 <i>N</i> NaCl. . . . .	197.714	0.000
	197.714	
Cell II—1-inch bright electrodes, 0.2 <i>N</i> NaCl . . . . .	84.260	
	84.254	
	84.259	
	84.256	0.007
Cell III—1-inch platinized electrodes, 0.2 <i>N</i> NaCl. . . . .	78.481	
	78.482	
	78.479	
	78.487	0.010

**Constancy of Resistances of Solutions in Cells Over Short and Long Time Periods.**—Dr. G. H. Gray's oscillograph measurements at 60 and 240 cycles and our conductivity data show that after two cycles the current does not cause an appreciable change in the resistance and capacity of the cell during short time periods such as ten minutes. It seemed desirable in the practical use of the conductivity method to see whether measurable changes occur in longer time intervals. Table III illustrates

TABLE III.—DATA SHOWING CONSTANCY OF RESISTANCES OF SOLUTIONS IN CELLS OVER LONG TIME PERIODS.

	Time.	Res. at 1000.	% change in R.	Time.	Res. at 600.	% change in R.
Cell I						
1" bright electrodes, 0.2 NaCl. . . . .	4.18	53.099	0.043	4.11	53.327	0.081
Next day. . . . .	9.36	53.122		9.45	53.370	
Cell II						
1" bright electrodes, 0.2 <i>N</i> NaCl. . .	11.46	84.187		12.19	84.444	
	4.08	84.200	0.044	4.04	84.460	0.055
Next day. . . . .	10.00	84.224		9.53	84.490	
Cell III						
1" platinized electrodes, 0.2 <i>N</i> NaCl	10.25	78.486		11.05	78.486	
	4.15	78.486	0.001	4.22	78.486	0.003
Next day. . . . .	10.12	78.487		10.22	78.488	
Cell V						
1/2" platinized electrodes, 0.2 <i>N</i> NaCl	3.38	89.143		3.59	89.156	
	9.35	89.144	0.001	9.40	89.156	0.000

some of our characteristic data, each measurement given being the average of a number of readings. These data show that in cells with platinized electrodes the resistances of the solutions do not change appreciably on standing in the cells for 24 hours. On the other hand in cells with bright platinum electrodes there is an increase in the resistance and the change seems to be larger when the resistance is measured at 600 cycles than when measured at 1000 cycles.

**A Comparison of the Resistances Obtained at 600 and 1000 Cycles by the Use of Inductance and Capacity to Balance the Capacity of the Cell.**—As was mentioned above, in order to obtain a perfectly sharp minimum in the telephone, the capacity in the cell must be accurately balanced by some method such as by another capacity in parallel with the resistance arm of the bridge, or by an inductance in series with the cell. Some measurements were made on resistances of solutions in different cells at 600 and 1000 cycles by using both methods of balance to see how closely the two would check. The data are shown in Table IV.

In order to use the substitution method with a condenser in parallel with the resistance arm,  $R_4$ , as in Fig. II, a balance was first made with the cell inserted, the cell was then removed and the substitution resistance,  $R_3$ , balanced against the resistances of the bridge. When this method is used a correction must be made on the substitution resistance according to the following equation worked out for us by Professor Edward Bennett:  $R_3/R_4 = R_1/R_2 - K/C$ , in which  $R_1$  and  $R_2$  are the values of the ratio coils,  $R_3$  the value of the substitution resistance,  $K$  the capacity in parallel with the resistance  $R_4$  which is necessary to balance the capacity of the cell, and  $C$  is the capacity of the cell calculated from the inductance, or by other methods which will be described later. When this correction is made for the three cases given in Table IV the values for the apparent resistances obtained by the use of an inductance and those obtained by the use of a condenser check extremely well. The largest variation is 0.004%, and in this case the data are not very satisfactory, but all of the remaining values check to within about 0.001%, which is not more than the experimental error.

The first part of the table gives the data for 0.2 *N* NaCl in Cell IX with roughened electrodes 2 inches in diameter. The readings were taken in the following order: First, Group 1, then Groups 2, 3, 4, etc. At both 600 and 1000 cycles the uncorrected resistance measured with the condenser is only about 0.002% higher than the one measured with the inductance, and the corrected resistances do not vary more than 0.001%. The second part of the table gives duplicate measurements, (a) and (b), of the data for 0.05 *N* NaCl in Cell I with 1-inch bright electrodes. Measurements were made in this case only at 1000 cycles. Here the uncorrected resistance measured with the condenser is about 0.013% higher than that measured

with the inductance, but the corrected resistances differ only 0.001%. The third part of the table gives the data on 0.025 *N* NaCl in Cell I at 600 and 1000 cycles. In this case there is practically no difference in the uncorrected readings with the condenser and inductance at 1000 but at 600 cycles the uncorrected resistance measured with the condenser is about 0.01% higher than that measured with the inductance. The corrected resistances, however, differ only 0.002% at 600 and 0.004% at 1000 cycles.

It will be seen from the data with both the condenser and the inductance that the apparent resistance decreases when the frequency is raised from 600 to 1000 cycles, which is in conformity with all of our other results. The changes in resistance obtained by using the 2-inch roughened electrodes with inductances or condensers were practically only 0.025%, whether corrected or not, because of the large capacity of these large electrodes. The 1-inch bright electrodes, with much smaller surfaces and capacities, however, showed a change of resistance of 0.0925% when the inductance method was used and 0.095% when we employed the corrected data from the condenser method. If the data are not corrected, however, this difference of 0.0025% experimental error becomes four times that large, namely, 0.010%. All of the above facts, then, show that both the inductance and the condenser methods give practically the same results when the proper corrections are made.

TABLE IV. -- A COMPARISON OF THE RESISTANCES OBTAINED BY THE USE OF INDUCTANCE AND OF CAPACITY TO BALANCE THE CAPACITY OF THE CELL.

Cell IX—0.2 *N* NaCl.

Inductance res. in ohms.		Condenser res. in ohms.	
600.	1000.	600.	1000.
282.159	282.088	282.166	282.098
(1) 282.161	282.090	(2) 282.169	282.097
282.163	282.092	282.168	
282.160	282.091		
282.162	282.092	282.166	282.096
282.163	282.094	282.167	282.095
(3)	282.095	(4)	282.096
	282.095		
	282.092		
	282.093		
282.162	282.091		282.096
(5) 282.163	282.091	(6)	282.097
Aver. before correction.....	282.162 282.092	282.167	282.096
Aver. after correction.....	282.162 282.092	282.162	282.094

Dif. in uncor. res by the two methods at both 600 and 1000, 0.002%.

Dif. in cor. res. by the two methods at 600, 0.000%.

Dif. in cor. by the two methods at 1000, 0.0007%.

Cell I.—0.05 <i>N</i> NaCl.			
Inductance res. in ohms 1000.		Condenser res. in ohms 1000	
(a).	(b).	(a).	(b).
197.715			
197.715			
197.717		197.740	
197.712		197.740	
197.713	197.711	197.740	
197.713	197.714	197.740	197.740
197.713	197.714	197.740	197.740
197.713	197.714	197.740	197.740
Aver. before correction.....	197.714    197.713	197.740	197.740
Aver. after correction.....	197.714    197.713	197.711	197.711
Dif. in uncor. res. by the two methods, 0.013%.			
Dif. in cor. res. by the two methods, 0.001%.			

Cell I.—0.025 <i>N</i> NaCl.			
Inductance res. in ohms.		Condenser res. in ohms.	
600	1000.	600.	1000.
	381.009		
	381.010		
	381.012		381.000
381.361	381.007	381.391	381.009
381.361	381.000	381.395	381.007
381.361	381.000	381.398	381.007
Aver. before correction.....	381.361    381.006	381.397	381.006
Aver. after correction.....	381.361    381.006	381.352	380.989
Dif. in uncor. res. by the two methods at 600, 0.010%.			
Dif. in cor. res. by the two methods at 600, 0.002%			
Dif. in uncor. res. by the two methods at 1000, 0.000%			
Dif. in cor. res. by the two methods at 1000, 0.004%			

### Conclusions.

(1) We have found that the Vreeland oscillator is the best and most convenient source of alternating current tried for conductivity work because (1) it is practically noiseless and can be started and stopped conveniently; (2) it gives practically a pure sine wave form; (3) it gives a constant frequency independent of the variation in the actuating direct current; and (4) this frequency can be changed easily to anything desired in our work.

(2) Curtis coils on porcelain spools should be used for all resistances above 10 ohms to prevent errors due to inductance and capacity effects.

(3) For greatest accuracy in balancing the bridge one should use a telephone which can be tuned to any desired frequency, and can be attached to a stethoscope, as suggested by Curtis.

(4) A substitution method suggested by Curtis for measuring resistances is advantageous as, by simply regulating the temperature of *R* in Fig. I, it prevents errors due to any changes in the resistances of the bridge

coils, or in the inductance, caused by variations in temperature, and allows the experimenter to read the resistances directly instead of having to make involved calculations.

(5) The bath, if made of metal, and also the bridge, should be grounded to prevent errors from capacity effects.

(6) In order to prevent changes in the resistance of the solutions during measurements the cells should be made (1) with the ground glass joints below the surface of the liquid of the bath to prevent evaporation of the solvent in the cell, (2) with the electrodes well supported by several glass arms and platinum posts to prevent changes in position of the electrodes, and (3) with the leads to the electrodes sealed off at the end in the glass tubes to allow the experimenter to keep these ends clean and to prevent changes in the resistance of the leads.

(7) Solutions should be made up and analyzed by weight methods in clean, resistance glass or quartz containers and transferred *under* the water of the bath into clean cells.

(8) Resistance measurements on a given solution in a given cell can be duplicated to within 0.001%.

(9) Resistance measurements on different parts of the same solution in the same cell, even when no special precautions were taken in filling the cell, checked to within 0.01%.

(10) The resistances of aqueous solutions in cells with platinized electrodes did not change appreciably on standing in the cells 24 hours. Cells with bright electrodes showed changes in resistance from 0.05 to 0.14% in 24 hours.

(11) A comparison of the resistances obtained by the use of (1) an inductance and (2) a condenser to balance the capacity of a cell shows that the values of the resistances obtained by the two methods are practically the same, the variation being only  $\pm 0.001\%$ .

MADISON, WIS.

WASHINGTON, D. C.

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[CONTRIBUTION FROM CHEMISTRY OF FOREST PRODUCTS, UNIVERSITY OF WISCONSIN.]

## STUDIES IN THE MEASUREMENT OF THE ELECTRICAL CONDUCTIVITY OF SOLUTIONS AT DIFFERENT FREQUENCIES.

### VII. INVESTIGATIONS ON THE TRUE AND APPARENT RESISTANCES, VOLTAGE, APPARENT CAPACITY, SIZE AND CHARACTER OF ELECTRODES, RATIO OF INDUCTANCE CHANGES TO RESISTANCE CHANGES, AND THE RELATION OF INDUCTION AND CAPACITY TO FREQUENCY.<sup>1</sup>

BY W. A. TAYLOR AND S. F. ACREG.

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In the preceding papers we have shown that the resistances of solutions of electrolytes can be measured with a precision of 0.001% and an

<sup>1</sup> We are indebted to the Carnegie Institution of Washington for aid in this work.

accuracy of 0.01% by the use of (1) Curtis resistances free from capacity and inductance; (2) a Vreeland oscillator giving a pure sine wave of uniform frequency which can be varied widely; (3) proper grounding and shielding of the electrical apparatus and the bath; (4) a telephone which can be tuned to any desired frequency; (5) cells whose electrodes are fixed and whose ground joints are immersed to prevent evaporation; and (6) the use of different bridge methods which give the same true electrical conductivities of the solutions.

In the present article<sup>1</sup> we will discuss chiefly (1) the relation of the resistances of solutions of electrolytes to the voltage, the frequency of the alternating current, and the area of the electrode surface; (2) the relation between the area of the electrode surface and the magnitude of the apparent "capacity" of the cell; (3) the relation between the electrolytes, electrode material, size and character of electrode surface, and change of inductance and resistance with change in frequency; (4) the measurement of the true electrical conductivity of solutions; (5) the explanation of the apparent "capacity" of the cell; (6) the relation between the inductances necessary to valence the capacity of the cell at different frequencies; and (7) the ratio of the change in resistance to the change in inductance produced by a change in frequency.

### Effect of Change of Voltage on the Apparent Resistance of Solutions of Electrolytes.

The first point to be investigated was the influence of change in voltage on the resistances of solutions in different cells. The bridge was first tested to see whether the resistances changed with change in voltage. It was found that a given resistance in the bridge did not vary as much as 0.001%, with change in voltage from one-eighth to 10 volts. Experiments along this line were carried out with the bridge coils alone, and also with inductances in two adjacent arms of the bridge.

We then took up the study of various solutions and in Table I are given the resistances of different solutions in several cells at a number of voltages. Each measurement given is the average of a number of readings. The range of voltage was from  $\frac{1}{4}$  to 2 v., at which the polarization voltage 1.23 is not reached at the electrodes. Above 4 volts there was in most cases such an appreciable heating effect that it was difficult to make accurate measurements. From an inspection of the data in Table I it is seen that the variation in the resistance is not more than  $\pm 0.001\%$ . This is true only when the cells, solutions and containers are kept scrupulously clean, as the slightest trace of grease or dirt causes a measurable

<sup>1</sup> Part of this work was done by Dr. Taylor at the Bureau of Standards, and we are indebted to Dr. J. L. Curtis for many valuable suggestions. We desire to express our thanks especially to Professor Edward Bennett of the the University of Wisconsin for the coöperation which will appear in joint articles later.



variation in the resistance with change in voltage. Since with unclean cells we have found variations in resistance as large as 0.08% when the voltage is changed from  $\frac{1}{4}$  to 2 v. constancy of resistance and inductance with change in voltage can be used as a very reliable test for cleanliness of cells and containers for the solutions.

TABLE I.—VALUES FOR THE RESISTANCES AND INDUCTANCES OF DIFFERENT SOLUTIONS IN VARIOUS CELLS, MEASURED AT DIFFERENT VOLTAGES.

			Res. $\frac{1}{4}$ v.	Ind. in $\mu$ h.	Res. $\frac{1}{2}$ v.	Ind. in $\mu$ h.	Res. 1 v.	Ind. in $\mu$ h.	Res. 2 v.	Ind. in $\mu$ h.
Cell I,	0.2	N NaCl..	53.099	280	53.099	280	53.098	280	53.099	280
	0.1	N NaCl..			101.108	315	101.109	315		
	0.05	N NaCl..			195.303	350	195.302	350		
	0.1	N KCl..	85.870	435	85.869	435	85.871	435		
Cell III,	0.2	N NaCl..	78.482	15	78.483	15	78.482	15	78.481	15
	0.2	N NaCl..	78.491	16	78.492	16	78.491	16		
	0.2	N NaCl..	78.481	13	78.480	13	78.479	13		
	0.1	N NaCl..			149.923	7	149.921	7		
Cell II,	0.2	N NaCl..	84.187	310	84.187	310	84.187	310		
	0.2	N NaCl..			84.260	380	84.259	380		
Cell V,	0.2	N NaCl..	89.143	40	89.143	40	89.143	40	89.143	40

These data also show that there is no change in the inductance necessary to balance the cell capacity and, therefore, no change in the capacity of the cell with this change in voltage. This would most probably not be true if we did not have a perfectly reversible system, for otherwise more ions would be discharged at one electrode than at the other during a given complete oscillation, and we would, therefore, expect the inductance to change. But even in perfectly reversible systems the constancy of resistance and of capacity, or inductance, with change in voltage below the polarization voltage 1.23 is one of the most important factors which must be considered in interpreting the "electrode phenomena." With a higher voltage at each pulse there is a greater number of electrons discharged, a greater change of concentration at the electrodes, the deposition of more gas ions on the electrodes, and a greater reverse contact potential, and Dr. G. H. Gray has now been able to show by oscillograph measurements that the resistance and capacity do not change with varying electrode potentials below the polarization voltage 1.23, but do change continuously above this point. Experiments to cover all phases of this problem are in progress.

#### Effect of Change of Frequency on the Apparent Resistance of Solutions of Electrolytes.

A study of the effect of change of frequency on the apparent resistance of electrolytes was next taken up. Acree and Robertson had noticed in their work that a change in the buzzer note caused a change in the apparent resistances of solutions in cells with bright electrodes. This point has doubtless been observed by many others and has recently been con-

firmed in conversations with Professor Mathews of the Department of Physical Chemistry in the University of Wisconsin, Dr. E. P. Wightman, and others. This naturally suggested the study of this phase of the problem, which, as far as we know, had never been investigated before 1909. and which is the most important phase of conductivity work.

We have studied solutions of different kinds and concentrations of electrolytes in cells differing in construction, size, and character of electrodes, etc. The frequencies used have been chiefly 600 cycles and 1000 cycles, although 60, 500, 2000 and 3000 were used in a few cases, and Mr. H. P. Hastings has now employed 60, 250, 500, 750, 1000, 1500, 2000 and 3000. In Table

TABLE II.

	Res. 1000 cycles.	Res. 600 cycles.	Dif. in res. at 1000 cycles and 600 cycles in Per cent.				
Cell II, 1" bright electrodes.							
0.2 <i>N</i> NaCl.....	84.256	84.541	0.337				
0.1 <i>N</i> NaCl.....	160.424	160.729	0.190				
0.03 <i>N</i> HCl.....	149.036	149.378	0.229				
0.1 <i>N</i> KCl.....	146.003	146.360	0.244				
0.05 <i>N</i> NaCl.....	310.202	310.544	0.110				
Cell II, 1" bright electrodes, silver plated.							
0.1 <i>N</i> NaCl.....	163.573	163.658	0.052				
0.1 <i>N</i> AgNO <sub>3</sub> .....	162.723	162.757	0.021				
Cell VI, 1" bright electrodes.							
0.2 <i>N</i> NaCl.....	11.492	11.803	2.635				
0.1 <i>N</i> NaCl.....	21.540	21.939	1.819				
0.05 <i>N</i> NaCl.....	41.052	41.476	1.022				
0.025 <i>N</i> NaCl.....	79.391	79.962	0.714				
Cell IV, 1/2" bright electrodes.							
0.2 <i>N</i> NaCl.....	146.930	148.720	1.203				
0.1 <i>N</i> NaCl.....	277.703	279.785	0.744				
0.05 <i>N</i> NaCl.....	534.40	536.30	0.355				
0.1 <i>N</i> KCl.....	241.24	244.17	1.200				
Cell XII, 2" cylindrical electrodes.							
0.005 NaCl.....	170.160	170.265	0.062				
0.001 <i>N</i> KI.....	81.623	81.685	0.076				
Cell III, 1" platinized electrodes.							
0.2 <i>N</i> NaCl.....	78.490	78.490	0.000				
0.1 <i>N</i> NaCl.....	149.922	149.922	0.000				
0.05 <i>N</i> NaCl.....	290.269	290.269	0.000				
0.2 <i>N</i> CuSO <sub>4</sub> .....	155.884	155.882	0.001				
0.1 <i>N</i> KCl.....	131.093	131.094	0.001				
Cell V, 1/2" platinized electrodes.							
0.2 <i>N</i> NaCl.....	89.143	89.156	0.015				
0.1 <i>N</i> NaCl.....	170.273	170.285	0.007				
0.05 <i>N</i> NaCl.....	329.769	329.770	0.000				
Cell IV, 1/3" bright electrodes.							
Frequency.....	250	500	750	1000	1500	2000	3000
Res.....	292.32	287.13	285.24	284.30	283.28	282.74	282.16
Ind. in Mili. hen....	21.79	6.19	2.95	1.90	0.98	0.64	0.21

II is given a summary of the values for the resistances of many different solutions in the same cells at 600 and 1000 cycles, and the difference between these two values in per cent. Each resistance given is the average of a number of readings. At the end of the table we have given the resistance and inductance measurements on 0.1 *N* NaCl in Cell IV at frequencies varying from 250 to 3000 cycles. These last measurements were made by Mr. H. P. Hastings.

From an inspection of these data it is seen that there is only a very small change in resistance with change in frequency from 600 cycles to 1000 cycles in the cells with *platinized* electrodes. With these cells it is also possible to get a balance with an accuracy of  $\pm 0.01\%$  without the use of either an inductance or condenser.

In the case of the cells with bright platinum electrodes, which must be used in some cases to prevent the decompositions caused by spongy platinum, there is a decrease in resistance with increase in frequency. This fact is shown particularly well by Mr. Hasting's data at the end of Table II. In this case the change in resistance with change in frequency from 250 to 3000 cycles is about 3.2%.

It is evident from the data that as the concentration of any given solution is decreased, and consequently the resistance is increased, in a given cell with bright electrodes, the change in resistance with change in frequency decreases. It, therefore, follows that the resistance should be made as high as possible and the voltage raised to get a good minimum, since the change in voltage used causes no change in the inductance or resistance. To accomplish this end, the solutions used in a given cell should be as dilute as possible and the electrodes should be at least 1 inch in diameter and 2 inches is preferable. If the resistance is above 10,000 ohms the errors will generally be less than 0.01% when the resistance at 1000 cycles is assumed to be the true resistance. In order to measure concentrated solutions, cells with constructions between the electrodes<sup>1</sup> should be used in order to make the resistance high.

It was also found that as the size of the electrode surface is increased the change in resistance with change in frequency decreases. This is best seen from Table III below, in which each measurement given is the average of a number of readings. We have selected cells and solutions giving as nearly as possible the same resistance so that the values may be comparable.

Table III also shows that as the surface of the electrodes is increased, the inductance necessary to obtain a balance decreases and hence the apparent "capacity" of the cell, acting as a condenser, increases. It is also seen that the higher the apparent capacity the lower the inductance

<sup>1</sup> Ref. to preceding article.

TABLE III.—MEASUREMENTS OF RESISTANCES AND INDUCTANCES ON SOLUTIONS HAVING ABOUT THE SAME RESISTANCES IN CELLS VARYING IN AREA OF ELECTRODE SURFACE.

	Res. at 1000 cycles.*	Ind. in $\mu h$ at 1000 cycles.	Res. at 600 cycles.	Ind. in $\mu h$ at 600 cycles.	Diff. in res. at 600 cycles and 1000 cycles in per cent.
Cell IV, $\frac{1}{2}$ " bright electrodes, 0.1 <i>N</i> NaCl...	277.703	2229	279.785	5849	0.744
Cell II, 1" bright electrodes, 0.05 <i>N</i> NaCl...	310.202	425	310.544	1295	0.110
Cell X, 2" bright electrodes, 2 <i>N</i> NaCl.....	421.200	134	421.489	326	0.068
Cell IX, 2" roughened electrodes, 0.2 <i>N</i> NaCl	282.092	115	282.162	310	0.025
Cell V, $\frac{1}{2}$ " platinized electrodes, 0.05 <i>N</i> NaCl	329.769	25	329.770	85	0.000
Cell III, 1" platinized electrodes, 0.05 <i>N</i> NaCl	290.269	0	290.2697	0	0.000

and hence the smaller the change in resistance with change in frequency. It is, therefore, evident that the electrical "capacity" of the cell should be made as large as possible. This may be done by increasing the surface area of the electrodes. It follows naturally that platinizing the electrodes best accomplishes this end. Spongy platinum may also increase the rapidity of the reversible ionization of molecular gas. We have found that solutions of different salts having about the same resistance in the same cell with platinum electrodes give approximately the same change in resistance with change in frequency from 600 cycles to 1000 cycles. This is shown in Table IV, in which each measurement given is the average of a number of readings.

TABLE IV.—RESISTANCE MEASUREMENTS ON SOLUTIONS OF DIFFERENT ELECTROLYTES HAVING APPROXIMATELY THE SAME RESISTANCES IN THE SAME CELLS.

	Res. at 1000 cycles.	Res. at 600 cycles.	Dif. in res. in per cent.
Cell II, 0.1 <i>N</i> NaCl....	164.024	164.404	0.23
0.03 <i>N</i> HCl....	149.036	149.378	0.23
0.1 <i>N</i> KCl....	146.003	146.360	0.24
Cell I, 0.2 <i>N</i> NaCl....	53.103	53.329	0.42
0.1 <i>N</i> HCl....	58.270	58.531	0.45

While this is true for platinum electrodes it is also apparent that there is a specific relation between the electrolytes, the electrode material, the character of the electrode surface, and the change of capacity and resistance with change in frequency. The above fact is shown in such data as the following in Table V. For this work the electrodes of one cell were plated electrolytically with silver. The oscillograph will also be used in these cases in the study of valve action and passivity.

TABLE V.—DATA SHOWING RELATION BETWEEN ELECTROLYTES, ELECTRODE MATERIAL, CHARACTER OF ELECTRODE SURFACE, AND CHANGE OF CAPACITY AND RESISTANCE WITH CHANGE IN FREQUENCY.

Character of electrode.	Solution.	Ind. in $\mu h$ .	Change in res. with change in frequency from 600 cycles to 1000 cycles.
1" bright platinum.....	0.1 <i>N</i> AgNO <sub>3</sub>	155	0.12%
1" rough, silver plated..	0.1 <i>N</i> AgNO <sub>3</sub>	25	0.012%
1" rough, silver plated...	0.1 <i>N</i> NaCl	95	0.052%

It is seen also that we have here the same relation between the inductance and the change in resistance with change in frequency as was noted above; that is, the lower the inductance and, therefore, the higher the capacity of the cell, the smaller the change in resistance with change in frequency.

**The Measurement of the True Electrical Conductivity of Solutions.**—In order to make accurate conductivity measurements, the cells and methods must be so perfected that the ratio of the resistances for any given solution in two cells, or of two solutions in any cell, must be constant to within 0.01%. This will not be the case unless we can eliminate electrode effects. We, therefore, compared two cells with platinized electrodes, in both of which the electrode effects have been shown to be zero or very small. Cell III has electrodes 1 inch in diameter and Cell V electrodes one-half inch in diameter. 0.2 *N*, 0.1 *N* and 0.05 *N* solutions of NaCl were measured in both cells and the ratios of the resistances calculated. The ratios are given in Table VI below, in which each measurement given is the average of a number of readings.

TABLE VI.—RATIOS OF THE RESISTANCES OF 0.2 *N*, 0.1 *N* AND 0.05 *N* NaCl MEASURED AT 1000 FREQUENCY IN TWO CELLS WITH PLATINIZED ELECTRODES.

	Res. of 0.2 <i>N</i> NaCl	Ratio of res.	Res. of 0.1 <i>N</i> NaCl	Ratio of res.	Res. of 0.05 <i>N</i> NaCl	Ratio of res.
Cell III.....	78.482		149.922		290.269	
Cell V.....	89.156	1.1360	170.285	1.1358	329.770	1.1361

The deviation in the ratio of resistances is only  $\pm 0.013\%$ , which is not much more than the experimental errors. We can, therefore, conclude that one inch *platinized* electrodes give nearly the true electrical resistance of these solutions when the resistance is above 100 ohms.

As it was found that the change in resistance with change in frequency of any solution in a cell with *bright* platinum electrodes becomes smaller and smaller as the frequency increases, we attempted to eliminate the "electrode effects," or polarization, and thus obtain the *true electrical resistance* of the solution, by extrapolating the resistances to infinite frequency. In order to do this measurements were made at three different frequencies, 600, 1000 and 2000 cycles, with two cells, both of which had electrodes 1 inch in diameter. The electrodes in Cell II were bright and in Cell III were platinized. 0.1 *N* and 0.05 *N* solutions of NaCl were used in each cell. We then plotted the results as curves<sup>1</sup> by using the resistances at different frequencies as ordinates and the reciprocal of the frequencies as abscissas. The points where these curves cut the X axis give approximately the values for the resistances at infinite frequency. The data used in plotting the curves are given in Table VII.

<sup>1</sup> The first calculations were made by Taylor and Curtis in *Physical Review*, 6, 61, following the suggestion by one of us.

TABLE VII.—RATIOS OF THE RESISTANCES OF 0.1 N AND 0.05 N NaCl MEASURED AT 60 CYCLES, 600 CYCLES, 1000 CYCLES, AND 2000 CYCLES IN TWO CELLS, ONE OF WHICH HAS BRIGHT AND THE OTHER PLATINIZED ELECTRODES 1 INCH IN DIAMETER, AND THE EXTRAPOLATION OF THESE RESISTANCES TO INFINITE FREQUENCY.

	Res. at 60 cycles.	Ratio of res. at 60 cycles.	Res. at 600 cycles.	Ratio of res. at 600 cycles.	Res. at 1000 cycles.	Ratio of res. at 1000 cycles.	Res. at 2000 cycles.	Ratio of res. at 2000 cycles.	Res. at $\infty$ cycle.	Ratio of res. at $\infty$ cycle.
Cell III, 0.1 N NaCl.	166.3 <sup>1</sup>		153.145		153.145		153.145		153.145	
0.05 N NaCl.	294.0 <sup>1</sup>	1.7679	293.092	1.91382	293.092	1.91382	293.092	1.91382	293.092	1.91382
Cell II, 0.1 N NaCl.	183.6 <sup>1</sup>		164.149		163.844		163.580		163.365	
0.05 N NaCl.	319.3 <sup>1</sup>	1.7396	313.491	1.90979	313.158	1.91132	312.895	1.91279	312.665	1.91390
Difference in ratios in $\frac{1}{C_1}$		1.60		0.21		0.13		0.05		0.004

<sup>1</sup> These solutions are different from those used in the remaining measurements and as neither set of solutions was made up at all accurately the resistance measurements for the two sets do not check; nevertheless, these solutions serve well for purposes of comparison of the difference between the ratios for bright and platinized electrodes.

TABLE VIII.—DATA SHOWING  $R_{\infty}$  CALCULATED BY MEANS OF THE EQUATION  $R_{\infty} = R_f - KLf$  AND THE DIFFERENCE BETWEEN THIS VALUE AND THAT OF  $R_{\infty}$  OBTAINED BY EXTRAPOLATING THE RESISTANCE TO INFINITE FREQUENCY.

	$R_{\infty}$ found by extrapolation.	Res. at 500.	Ind. at 500 in mh.	$R'_{\infty}$ calc.	% dif. in $R_{\infty}$ and $R'_{\infty}$ .	Res. at 1000.	Ind. at 1000 in mh.	$R'_{\infty}$ calc.	% dif. in $R_{\infty}$ and $R'_{\infty}$ .
Cell 1 <sub>2</sub> , bright Pt elec., 0.2 N NaCl	147.45	150.98	3.76	147.56	+0.07	149.20	0.99	147.30	-0.10
Cell 1 <sub>2</sub> , bright Pt elec., 0.1 N NaCl	164.30	165.42	1.09	164.42	+0.07	164.90	0.28	164.39	+0.05
Cell 2 <sup>1</sup> , etched Pt elec., 0.1 N NaCl	455.42	455.74	0.38	455.40	-0.004	455.61	0.13	455.37	-0.01
Cell 1 <sup>1</sup> , etched gold elec., 0.2 N NaCl	101.58	102.39	0.84	101.62	+0.04	102.02	0.22	101.62	+0.04

It is seen that the ratios of the resistances of these solutions in the two cells varied 1.62% at 60 cycles, 0.21% at 600, 0.13% at 1000 and 0.05% at 2000. As the resistances in cells with platinized electrodes do not change with change in frequency from 600 to 2000 cycles the resistance at infinite frequency would in all probability be the same as at the lower frequencies. By comparing the ratios for the two cells at infinite frequency the difference is only 0.004%, which is not more than the errors involved in the experiments and the extrapolation. We must, therefore, conclude that cells with bright platinum electrodes give approximately the true electrical conductivity of solutions only at high frequencies approaching infinity.

In order to eliminate the necessity of making resistance measurements at several different frequencies and extrapolating the resistance to infinite frequency to obtain the true electrical resistance of solutions of electrolytes, we have been able to derive an equation by which the resistance at infinite frequency can be calculated approximately from the resistance and inductance measurements at any given frequency. Professor Bennett has developed the full equations for expressing the changes in the apparent resistance and capacity of a system behaving like a cell, namely, a resistance in series with a "leaky" condenser. In his equations the value of  $n$  in the function ( $f^n$ ) varies with frequency and our value ( $f^1$ ) seems to hold approximately for our frequencies from 250 to 3000.

By using the equation  $(R_f - R_\infty)/L_f f = K$ , when  $R_f$  and  $L_f$  are the resistance and inductance (millihenries) measurements, respectively, at any given frequency,  $f$ ,  $R_\infty$  the resistance at infinite frequency, and  $K$  a constant, we have calculated the value of  $K$  and found it to be about 0.00182. In order to obtain this constant we have used several different solutions in various cells. Cells with bright and etched platinum, and etched gold and silver electrodes were used, as with these we obtain the largest values for  $L_f$  and  $R_f - R_\infty$  and thus minimize the errors.

By using this value for  $K$  and substituting the values for  $R_f$ ,  $L_f$ , and  $f$  at 250, 500, 750, 1000, 1500 and 2000 cycles, in the equation  $R_\infty = R_f - KL_f f$  we then calculated the resistance at infinite frequency,  $R_\infty$ , for several different solutions in different cells, many of which were not used in obtaining the constant  $K$ . A few of the data for frequencies of 500 and 1000 are given in Table VIII in this article. The values for  $R'_\infty$  calculated by using the equation differ by only 0.01 to 0.10%, from those for  $R_\infty$  obtained by extrapolation even though  $R_f$  differs from  $R_\infty$  as much as 2.4% in some cases. The average of the values for  $R'_\infty$  by using ALL of the above frequencies for any given cell and solution varied only from  $\pm 0.01$  to  $\pm 0.025\%$  from those obtained for  $R_\infty$  by extrapolating the resistance to infinite frequency and will be reported in detail in another article on the development of these equations. This gives us a

method for determining approximately the true electrical resistance of the solution by measuring the "apparent" resistance and the inductance (or capacity) at any one frequency. The apparent resistance at 1000 cycles will be within 0.01% of the true resistance if the solution used in the given cell is so dilute that the inductance in henries is less than  $0.5 \times 10^{-4}$  times the resistance. It is thus a simple matter to tell approximately how dilute the solution must be in a given cell to give the true resistance within 0.01% at 1000 cycles.

Another way to get the true resistance within 0.01% at 1000 (1500) cycles is to make use of the fact discussed above that the difference between the apparent resistances at 500 and 1000 cycles, or at 750 and 1500 cycles, is exactly the difference between the true resistance and the apparent resistance at 1000 (1500) cycles. For a given cell, therefore, we measure once for all what resistance is needed to make  $R_{500} - R_{1000}$  or  $R_{750} - R_{1500}$  less than 0.01% of  $R_{1000}$  or  $R_{1500}$  and always employ solutions giving about that resistance or more. This procedure avoids the use of standard inductances or capacities.

The change in resistance with change in frequency shown above will make it clear why different careful workers have found different values for the molecular conductivity and ionization of the same carefully prepared solution of the same salt, as some measurements were made at 60 cycles, others at 1000 cycles, etc. In calculating the ionization the equation  $\alpha = \mu_v/\mu_\infty$  is used. In obtaining  $\mu_v$ , cells with small electrodes are ordinarily used and often the resistances are comparatively small. It has been shown above that the error in such cases may be from 3 to 4%. On the other hand, in obtaining  $\mu_\infty$  cells with large electrodes placed close together are ordinarily used and the resistances are usually large. In such cases the error will be small, such as from 0.05 to 0.1%. It is thus seen that large errors may occur in  $\mu_v$  and hence in  $\alpha$ , and that the extent of this error will depend on the resistance and on the frequency used in making the measurement. In all cases  $\alpha$ ,  $\mu_v$  and  $\mu_\infty$  should be extrapolated to infinite frequency to obtain correct values.

#### **The Effect on the Capacity of Deposition of Gas on the Electrodes.**

—When a current passes in one direction in an aqueous solution of a salt, for instance, a metal or hydrogen is deposited at one electrode and an anion or oxygen at the other. These gases can either remain on the plates, thus decreasing their surface and increasing the resistance and inductance, or dissolve in the water, or become ions on the reverse pulse of the current. A study of these points is being made by Mr. H. P. Hastings by saturating the electrodes and the liquid around the electrodes with  $H_2$ ,  $O_2$ , etc., by pumping out the solution before and during electrolysis and by adding nonelectrolytes (and electrolytes) to combine with the gases. Experiments which have been carried out up to this time apparently show that



the changes in resistance and inductance with change in frequency cannot be accounted for by the deposition of neutral gases on the electrodes, but are probably due to a concentration of the ions of the electrolyte and solvent at and on the electrode and hence to an attendant contact potential.

That the changes are not due to gas deposited on the electrodes is shown by the data in Table IX. These measurements were made at 60 cycles because we would expect the greatest changes in capacity to occur at low frequencies. We shall, however, investigate this subject at higher frequencies of 1000, 1500, etc., where settings can be made with much higher accuracy.

TABLE IX.—DATA SHOWING EFFECT ON THE CAPACITY OF DEPOSITION OF GAS ON THE ELECTRODES.

Cell V,  $1/2$ " platinized electrodes.

Solution.	Res. in ohms.	Ind. in $\mu$ h.
0.1 <i>N</i> NaCl, before passing H through cell.....	147.98	5.9
H passed through cell 2 min.....	147.98	5.9
H passed through cell 2 min.....	147.93	5.5
0.05 <i>N</i> NaCl.....	306.4	6.2
H passed through cell 2 min.....	306.5	6.2
H passed through cell 10 min.....	306.5	5.9
H passed through cell 20 min.....	306.5	6.2
H passed through cell and solution 30 min.....	306.0	5.9

If the electrode phenomena are not due to deposited neutral gas it seems likely that they arise from a double layer formed by the deposition of the ions of the solvent and solute on the electrode and by the change in concentration of the electrolyte at the electrode. If this is the case we should expect these changes to be so closely connected with the electrical factors that very definite relations should be found (1) between the inductances and the frequencies, and (2) between the change in resistance and the corresponding change in inductance produced by changes in frequency. That these relationships are very definite is shown in the next two sections.

**Relation between the Inductances Necessary to Balance the Capacity of the Cell at 600 and 1000.**—By a study of both water and alcoholic solutions in nine different cells it was found that the inductance necessary to balance the capacity of the cell is much larger at 600 than at 1000 cycles and that the inductance is nearly inversely proportional to the square of the frequency. This is shown by the data given in Table X. The average of fifty values for the calculated ratio is 2.66 while the value for the ratio of the square of the frequencies is 2.77. As this relation holds true for a "leaky" condenser the cell seems to act as a simple condenser with a leak.

**Ratio of Change in Resistance to Change in Inductance Produced by a Change in Frequency.**—All of the data given above show that as

TABLE X.—DATA GIVING THE RATIO OF INDUCTANCES NECESSARY TO BALANCE THE CAPACITY OF THE CELL.

		Ind. in $\mu$ h.		
		600.	1000.	Ratio.
Cell I, 1" bright electrodes,	0.2 <i>N</i> NaCl.....	715	280	2.55
	0.1 <i>N</i> NaCl.....	835	315	2.65
	0.05 <i>N</i> NaCl.....	915	350	2.61
	0.025 <i>N</i> NaCl.....	1045	395	2.65
	0.2 <i>N</i> AgNO <sub>3</sub> .....	560	210	2.67
	0.1 <i>N</i> KI (alc.).....	1500	580	2.58
Cell IV, 1" bright electrodes,	0.2 <i>N</i> NaCl.....	6138	2272	2.70
	0.1 <i>N</i> NaCl.....	5849	2229	2.62
	0.1 <i>N</i> KI (alc.).....	6700	2500	2.68
Cell IX, 2" sand blasted electrodes,	0.2 <i>N</i> NaCl.....	310	115	2.70
Cell XI, cylindrical electrodes, 1/2" long,	0.001 <i>N</i> KI....	2450	910	2.69
Cell XII, cylindrical electrodes, 2" long,	0.0005 <i>N</i> NaCl....	475	175	2.71
	0.001 <i>N</i> KI.....	365	145	2.52

the frequency of the alternating current approaches infinity, the change of resistance of a given solution in a given cell, and also the inductance necessary to balance the capacity of the cell, approach zero. In Table XI are given the resistances at 1000 cycles, the differences between the inductances in millihenries and the differences between the resistances in ohms at 600 and 1000 cycles, and the ratios of the differences in inductance to the difference in resistance. It will be seen that the ratios are very close to a constant 2.0. A few of the values calculated for different solutions in different cells are given in Table XI below. Many other cells of different types give this same constant, as they should theoretically.

TABLE XI.—DATA SHOWING RATIO BETWEEN THE DIFFERENCE IN RESISTANCE AND THE DIFFERENCE IN INDUCTANCE WITH CHANGE IN FREQUENCY FROM 600 TO 1000 CYCLES ON A GIVEN SOLUTION IN A GIVEN CELL.

	Res. at 1000.	Dif. in Ind. in $\mu$ h.		Dif. in R in ohms.	$\mu$ h/ohms.
Cell I, 1" bright electrodes.	0.2 <i>N</i> NaCl. ....	53.103	0.435	0.226	1.925
	0.1 <i>N</i> NaCl. ....	101.108	0.520	0.250	2.080
	0.05 <i>N</i> NaCl. ....	195.302	0.565	0.276	2.050
	0.025 <i>N</i> NaCl. ....	381.005	0.650	0.356	1.826
	0.2 <i>N</i> AgNO <sub>3</sub> . ....	54.521	0.350	0.176	1.990
	0.03 <i>N</i> HCl. ....	149.251	0.630	0.340	1.853
	0.1 <i>N</i> KI. ....	130.134	0.790	0.350	2.260
	0.1 <i>N</i> KI (alc.) ....	609.263	0.920	0.520	1.770
Cell II,	0.2 <i>N</i> NaCl. ....	84.259	0.605	0.289	2.093
	0.1 <i>N</i> NaCl. ....	160.424	0.600	0.305	1.970
Cell IV,	0.05 <i>N</i> NaCl. ....	534.400	3.866	1.900	2.030
Cell VI,	0.2 <i>N</i> NaCl. ....	11.492	0.635	0.311	2.040
	0.1 <i>N</i> KI (in alc.) ....	90.000	0.930	0.468	1.990

Considering the fact that most of this work was done before the method was finally perfected, the values are remarkably constant. Mr. H. P.

Hastings has now secured much more elaborate data confirming these results at widely different frequencies, resistances, capacities, and inductances, and we have devised some simple equations for developing the theoretical aspects and for correlating these phenomena approximately, especially with the equation  $R_{\infty} = R_f - KL_f f^n$  discussed above.

**Apparent Capacities of Various Solutions in Different Cells.**—In Table XII we have given the values in microfarads for the capacities of several different solutions in different cells at both 600 and 1000 cycles, calculated from the inductance measurements by means of the equation  $C = 1/L\omega^2$ . These data show that the values for the cells with platinized electrodes are very high, and also that the values for the capacities at the two frequencies are nearly the same. It is also seen that the values for the cells with platinized electrodes do not check very satisfactorily and this is due to the fact that  $L$  is very small and thus a small error in  $L$  causes a very large change in  $C$ .

TABLE XII.—CAPACITIES OF DIFFERENT SOLUTIONS IN VARIOUS CELLS AT 600 AND 1000 CYCLES, CALCULATED FROM THE EQUATION  $C = 1/L\omega^2$ .

Solution.		C in $\mu f.$ at 600 cycles.	C in $\mu f.$ at 1000 cycles.
Cell V, $\frac{1}{2}$ " platinized electrodes,	0.2 N NaCl.....	787	633
Cell II, 1" bright Pt electrodes,	0.2 N NaCl.....	88	82
Cell VI, 1" bright Pt electrodes,	0.2 N NaCl.....	68	63
Cell III, 1" platinized electrodes,	0.1 N NaCl.....	5405	3623
Cell V, $\frac{1}{2}$ " platinized electrodes,	0.1 N NaCl.....	781	725
Cell II, 1" bright Pt electrodes,	0.1 N NaCl.....	70	72
Cell VI, 1" bright Pt electrodes,	0.1 N NaCl.....	53	50
Cell III, 1" platinized electrodes,	0.05 N NaCl.....	..	..
Cell IV, $\frac{1}{2}$ " bright Pt electrodes,	0.05 N NaCl.....	12	11.5
Cell II, 1" bright Pt electrodes,	0.05 N NaCl.....	55	59
Cell X, 2" bright Pt electrodes,	0.05 N NaCl.....	213	190
Cell IX, 2" etched Pt electrodes,	0.05 N NaCl.....	227	222
Cell V, 1" platinized electrodes,	0.05 N NaCl.....	826	1010

In Table XIII are given the values for the capacities of several different solutions in various cells calculated from the equation (1)  $C = 1/L\omega^2$ , and (2)  $C^2 - C/L\omega^2 = -1/R_3^2\omega^2$ , which latter equation will be discussed more fully in a later paper. The values calculated for the capacity by the two methods check very well.

The changes of concentration of the electrolyte at the electrode and the deposition of ions on the electrodes both doubtless give rise to the reverse electromotive force which makes the cell act like a condenser and diffusion and neutralization phenomena make the condenser "leak." Professor Bennett has devised equations for treating such phenomena mathematically and a full report on this subject will be given later.

The most important part of our work planned is to study the electrode phenomena and the phase relations. In order to do this we are devising

TABLE XIII.—CAPACITIES OF DIFFERENT SOLUTIONS IN VARIOUS CELLS CALCULATED

FROM THE EQUATIONS (1)  $C = \frac{I}{L\omega^2}$ , (2)  $C^2 = \frac{C}{L\omega^2} = -\frac{I}{R_3^2\omega^2}$ .

Cell.	Solution.	Res. at 600 cycles.	Ind. at 600 cycles. 1000 in $\mu$ h.	Res. at 1000 cycles.	Ind. at 1000 cycles in $\mu$ h.	Cap. in $\mu$ f. $C = \frac{1}{L\omega^2}$ .	Cap. in $\mu$ f. $C^2 = \frac{C}{L\omega^2} = -\frac{1}{R_3^2\omega^2}$ .
IV	0.2 N NaCl	148.7	6138	.....	.....	11.5	11.3
IV	0.1 N NaCl	280.0	5849	.....	.....	12.0	12.2
IV	0.1 N NaCl	.....	.....	277.7	2230	11.4	11.3
IV	0.05 N NaCl	536.3	4752	.....	.....	15.0	15.0
II	0.2 N NaCl	84.4	800	.....	.....	88.0	88.0
II	0.05 N NaCl	310.5	1295	.....	.....	55.0	55.5
VII	0.1 N NaCl	29.0	990	.....	.....	72.0	70.5
VIII	0.1 N NaCl	43.5	1210	.....	.....	58.0	58.8
IX	0.2 N NaCl	282.0	310	.....	.....	227.0	229.0

alternating current potentiometer methods to study the electromotive force and phase changes near the electrodes. We are using some cells with very small movable plate and point electrodes which are brought close together to magnify the electrode effects and are devising other cells with plane parallel electrodes which can be adjusted as close together as desired by interferometer methods, and we can thus make the known distance between the electrodes so small that the ions move from one plate to the other and back at each cycle and make the electrode phenomena play the chief role. Professor Bennett has available a very fine triple oscillograph with a period of 0.0003 second, with which it is possible to detect and measure changes in phase, voltage, current, capacity, and other phenomena in very short-time periods and at different frequencies, and Dr. G. H. Gray has already made important studies which will be reported later in detail.

### Conclusions.

(1) There is no measurable change in the resistance of a solution, or the inductance, with the change in voltage needed, provided the cells, solutions, and containers are kept scrupulously clean. If the cells are not clean, however, there is a change in resistance with change in voltage, and this fact can be used as a very reliable test for cleanliness of cells.

(2) In order to make accurate conductivity measurements the cells and methods must be so perfected that the ratios of the resistances for any given solution in two cells or of two solutions in any cell, must be constant to within 0.01%. This will not be the case unless we can eliminate electrode effects. The ratios of the resistances of 0.2 N, 0.1 N and 0.05 N NaCl in two cells, one with 0.5 and the other with 1 inch *platinized electrodes* did not vary more than 0.01% which is about the experimental error shown to be due to the 0.5 inch electrodes and other causes. Since there is no measurable change in the resistance of a solution with change in frequency around 500 to 2000 cycles in our cells *with platinized*

*electrodes* 1 inch or more in diameter, we can, therefore, conclude that one-inch platinized electrodes give approximately the true electrical resistance of these solutions at such frequencies, and certainly do so at infinite frequencies, if the resistance is above 100 ohms.

(3) In cells with *bright platinum electrodes* there is a change in resistance with change in frequency from 600 to 1000 cycles and higher, and this change depends upon several factors: (1) as the concentration of any given solution is decreased, and, therefore, the resistance increased, the change in resistance with change in frequency is decreased; (2) as the area of the electrode surface is increased the change in resistance with change in frequency is decreased; (3) as the area of the electrode surface is increased the inductance necessary to obtain a balance is decreased, and, hence the apparent "capacity" of the cell is increased. (4) The higher the apparent "capacity" of the cell, and, therefore, the smaller the inductance necessary to balance this capacity, the smaller the change of resistance with change in frequency becomes. As the apparent "capacity" of a cell is increased by increasing the surface, platinized electrodes should give the smallest change in resistance with change in frequency and this is borne out by all our data. (5) Solutions of different salts having about the same resistance in the same cell with bright platinum electrodes give approximately the same change in resistance with change in frequency from 600 cycles to 1000 cycles. (6) There is a specific relation between the electrolyte, the electrode material, the character of the electrode surface and the change of capacity and resistance with change in frequency. This is shown by the fact that for a change in frequency from 600 cycles to 1000 cycles. 0.1 *N*  $\text{AgNO}_3$  in a cell with 1 inch bright platinum electrodes gives a change of 0.12%; 0.1 *N*  $\text{AgNO}_3$  in this cell with the 1-inch electrodes, rough, silver plated, gives a change of 0.012%, and 0.1 *N*  $\text{NaCl}$  in the same cell a change of 0.052%.

By comparing the resistances of 0.1 *N* and 0.05 *N*  $\text{NaCl}$  in two cells, one of which had bright and the other platinized electrodes one inch in diameter, it was seen that the ratio for the cell with bright electrodes was much lower at the lower frequencies than that for the cell with platinized electrodes, but as the frequency was increased the ratio for the cell with bright electrodes approached that for the cell with platinized electrode. Extrapolating the resistance for the cell with bright electrodes to infinite frequency the ratio was found to differ by only 0.004% from that given by the cell with platinized electrodes. It is thus shown that the true electrical resistance of solutions can be measured in cells with bright platinum electrodes only at infinite frequency. We, therefore, recommend for all conductivity work involving an accuracy of 0.01% the use of a Vreeland oscillator, giving three or more frequencies, for example, 500, 750, 1000

and 1500, or 2000 cycles, and the extrapolation of the corresponding resistances to that at infinite frequency.

(4) By substitution in the equation  $(R_f - R_\infty)/L_f f = K$ , where  $R_f$  and  $L_f$  are the resistance and inductance measurements, respectively, at any given frequency  $f$ ,  $R_\infty$  the resistance at infinite frequency, and  $K$  a constant, we can calculate  $R_\infty$  for any given cell and solution. The values found for  $R_\infty$  by this equation differ from those found by extrapolation by only  $\pm 0.01$  to  $\pm 0.025\%$ .

(5) The fact that there is a change in the resistance of electrolytes with change in frequency makes it clear why different workers have found different values for the molecular conductivity and ionization of the same solution, as some measurements were made at 60 cycles, others at 1000 cycles, etc. The resistances or conductivities at *infinite frequency* should be used in all cases.

(6) Saturation of bright and platinized electrodes with hydrogen produces no appreciable change in the "capacity" of the cell at 60 cycles. This and a great deal of other evidence seems to show that the "capacity" does not arise simply from a neutral gas layer deposited on the electrodes and acting as an air condenser. It is probably due to a "double layer" of ions of the electrolyte and of the solvent at and on the electrodes and hence to "contact potential" by these changes of concentration arising from electrolysis.

(7) The ratio between the inductance measurements at 600 and 1000 cycles with various solutions in many different cells is a constant, the value being about 2.66. This shows that the inductance is nearly inversely proportional to the square of the frequency, the ratio for the square of the frequency used being 2.77. As this relation holds true for a leaky condenser the cell seems to act as a resistance in series with a simple condenser with a leak.

(8) As the frequency of the alternating current is increased the change in apparent resistance of a given solution in a given cell, and also the inductance necessary to balance the capacity of the cell, are decreased and both approach zero at infinite frequency. It was found that the ratio of the difference in the inductance in millihenries to the difference in the resistance in ohms between 600 and 1000 is a constant, being about 2.00.

(9) The electrical capacities of the cells acting as leaky condensers have been measured by different consistent bridge methods. The capacities vary with the solution, size of electrode, character of surface, resistance, and other factors, and range from 10 to 1000 microfarads for bright electrodes and from about 500 to 5000 microfarads for platinized electrodes.

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## THE MEASUREMENT OF ELECTROLYTIC CONDUCTIVITY. I. THE THEORY OF THE DESIGN OF CONDUCTIVITY CELLS.

BY EDWARD W. WASHBURN.

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TABLE OF CONTENTS.—Nomenclature. 1. Introduction. 2. The Bridge Assembly. 3. The Distribution of the Current in the Bridge Network. 4. The Theory of Cell Design. 5. The Adjustment of the Total Current through the Bridge for a Conductance Measurement. 6. Summary. 7. Numerical Values of the Variables which Control the Cell Design. 8. Types of Conductivity Cells. 9. A Series of Cells Covering the Complete Conductance Range for Aqueous Solutions. 10. A Cell with a Minimum Volume Factor. 11. Connecting the Cell to the Bridge. 12. The Temperature Coefficient of the Cell Constant of a Conductivity Cell. 13. The Choice of the Material for Constructing a Conductivity Cell. 14. The Elimination of Polarization.

### NOMENCLATURE.

$A$	Area of the cross-section between the electrodes.	$\phi_T$	= $\phi$ , Percentage error due to heating of the cell during the measurement.
$a$	= $\phi^3 \frac{ds}{\alpha}$	$R$	Resistance of the cell = that of the resistance box.
$b$	= $I_T^2 t$	$R_B$	Resistance of the slide wire with its extension coils.
$C$	Capacity	$R_T$	Resistance of the telephone.
$C_p$	Capacity equivalent of polarization.	$R_{\min.}$	Minimum resistance which the cell may have.
$c$	= $R_B + 4R_T$	$R_{\max.}$	Maximum resistance which the cell may have.
$d$	Density of the solution.	$r$	Range-ratio for the cell.
$f$	Frequency of the alternating current.	$s$	Specific heat capacity of the liquid in the cell.
$I$	Total current through the Wheatstone bridge network.	$\Delta T$	Rise in temperature of the cell during the passage of the current.
$I_A$	Current through the conductivity cell.	$\Delta T'$	Fluctuation in the temperature of the bath containing the cell.
$I_T$	Audibility current of the telephone.	$t$	Time required to obtain the bridge setting (sec.).
$j$	= $\sqrt{-1}$	$Z$	Impedance of the cell.
$k$	Dielectric constant of the liquid in the cell.	$\alpha$	Temperature coefficient of the conductance of the liquid in the cell.
$K$	Cell constant.	$\beta$	Coefficient of thermal expansion (linear) of the material of which the cell is constructed.
$\bar{L}$	Specific conductance of the solution.	$\gamma$	Coefficient of expansion of platinum.
$l$	Distance between the electrodes of the cell.	$x_C$	Condensive reactance.
$p$	Percentage error due to the uncertainty in determining the correct bridge setting.	$x_L$	Inductive reactance.
$\phi_L$	Percentage error due to lead resistance.		
$\phi_K$	Percentage error in the cell constant.		

**1. Introduction.**—Since the appearance in 1898 of Kohlrausch and Holborn's "Leitvermögen der Elektrolyte," no comprehensive treatment of the theory and practice of conductance measurements in the case of solutions of electrolytes has appeared. During the period which has elapsed since Kohlrausch's pioneer work in this field the advances in experimental methods and apparatus have made possible a very great improvement in the precision attainable in such measurements and have also led to a more perfect understanding of some of the sources of error and the precautions necessary for their elimination.

Briefly stated the problem of improving the accuracy of the Kohlrausch apparatus for measuring the conductivity of electrolytes is simply a problem of selecting the parts of the apparatus and so disposing them with respect to one another that the whole Wheatstone bridge assembly shall approach as nearly as possible the ideal assembly required by the theory of the alternating current bridge. The principle alterations required in the apparatus itself are (1) the substitution of a high frequency generator giving a pure sine wave of a single frequency, in place of the induction coil; (2) the use of a telephone tuned to the frequency employed; (3) the use of resistance units free from inductance and capacity; and (4) a proper and efficient use of the principle of electromagnetic shielding. A number of other minor improvements have also been made but those just stated are the fundamental changes required by theory.

The writer's first successful experiments with an apparatus incorporating all of the first three changes mentioned above were made in the Fall of 1911, and a preliminary paper describing the advantages of the improved apparatus was published in *THIS JOURNAL* in February, 1913. Since then a number of other improvements have been made in the details of construction and arrangement of the cells and the bridge and a description of some of these can be found in Cat. 48 of the Leeds & Northrup Company, which was published in May, 1915.

In developing the improved apparatus the writer has been ably assisted by his students, especially by Dr. J. E. Bell and Mr. Karr Parker with whose assistance most of the experimental work has been carried out. It had been the writer's intention to incorporate the results of the investigations in this laboratory in a monograph which would deal rather exhaustively with the whole subject of the electrical conductivity of solutions, but owing to the transfer of the writer's activities to a new field the project will have to be abandoned. The present series of papers will, therefore, deal only with the theory of the construction, assembly and use of the apparatus as finally perfected.

As an apparatus for accomplishing its purpose it is now perfect, in the respect that the degree of precision attainable in the measurements is governed and limited solely by the accuracy with which the temperature



of the constant temperature bath containing the cell can be controlled. All other sources of error which affect the precision of the measurement are negligible in comparison with this one.

The present paper deals only with the design, construction and use of the conductivity cells. The two following papers will be devoted to a discussion of the telephone as an indicating instrument and to the make-up and arrangement of the bridge assembly, respectively.

**2. The Bridge Assembly.**—With regard to its behavior towards an alternating current, an electrolytic cell together with its lead wires may be considered as a resistance and a capacity in series, shunted by a condenser.<sup>1</sup> In practice, however, the influence of polarization, which has the effect of a capacity in series with the cell, is usually eliminated by employing platinized electrodes or by using a sufficiently high frequency, or both, and hence in nearly all cases this factor may be neglected. Under these circumstances the cell and its connecting wires may be regarded as a resistance shunted by a condenser.<sup>2</sup>

In measuring the conductance of such a cell with the aid of a Kohlrausch slide-wire bridge, one of the arms of the bridge contains a variable

<sup>1</sup> Or according to Wien (*Ann. Phys.*, **58**, 67 (1906)) as a resistance in parallel with a condenser and in series with a capacity. For the cases considered in this paper the two arrangements become identical.

<sup>2</sup> Assuming that its specific inductive reactance is negligible in comparison with its specific condensive reactance (the value of  $x_L$  for a water cell—Type A—exclusive of the platinum leads, is only about 0.0002 microhenry), the specific admittance of an aqueous solution for a frequency of 1000 cycles is practically equal to  $\sqrt{0.197 \cdot 10^{-14} + \bar{L}^2}$  reciprocal ohm. Evidently the admittance does not differ appreciably from the conductance until the latter falls to a very low value. Thus for  $L = 10^{-6}$  (ordinary conductivity water) the admittance differs from the conductance only by 0.1%. The dielectric condensive reactance of the conductivity cell itself is thus ordinarily a *very small* quantity. Practically all of the reactance usually ascribed to the cell is due to the leads which connect it to the bridge. The general expression for the impedance of a non-polarizable cell and its leads is

$$Z = \sqrt{\frac{(R^2 + x_L^2)x_C^2}{(x_C - x_L)^2 + R^2}}$$

Evidently, therefore, the residual reactance may be either inductive or condensive according to the arrangement of the leads. The best arrangement is twisted or twin wire leads and under these circumstances the residual reactance is condensive and the above expression reduces to

$$Z = \frac{Rx_C}{\sqrt{R^2 + x_C^2}}$$

which is an expression of the same form as that for the cell alone. In other words the condensive reactance of the twisted leads can be treated practically as though it were part of the dielectric condensive reactance of the cell. By using leads of the same length and form on both sides of the bridge the residual condensive reactance will ordinarily be on the side of the cell and the variable air condenser will then be connected across the terminals of the variable pure resistance as shown in Fig. 1.

known resistance. We shall assume that this resistance is free from both inductance and capacity and that a variable capacity is employed in parallel with it. These are the ideal conditions and are the ones which should be approximated at least, in practice.

With this understanding the ideal Wheatstone-bridge network may be represented diagrammatically by Fig. 1. A slide-wire having the re-

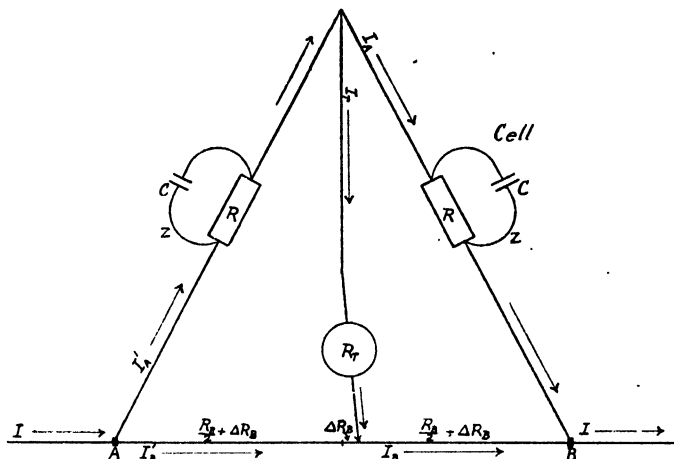


Fig. 1.—Diagrammatic representation of the ideal Wheatstone-bridge network containing a conductivity cell free from polarization.

sistance  $R_B$  is stretched between the points  $A$  and  $B$ . The sine-wave alternating current  $I$  of a single frequency  $f$  will be considered as entering at  $A$  and dividing as indicated by the arrows. The left arm of the bridge contains the variable resistance  $R$  shunted by the variable capacity  $C$  (an air condenser), the impedance of this arm of the bridge being  $Z$ . The current through this arm of the bridge is  $I_A'$ . The other arm of the bridge contains the cell, of resistance  $R$  and having a condensive reactance<sup>2</sup> equivalent to that which would result from a capacity  $C$  in parallel with the resistance  $R$ . The impedance of this arm of the bridge will be  $Z$  and the current through it will be  $I_A$ . It will be noticed that this arrangement brings the bridge setting *in the center of the wire*, where it should be in all accurate work in which a slide-wire bridge of the type indicated is employed.

A tuned telephone having the resistance  $R_T$  connects the sliding contact with a point between the cell and the resistance box as indicated. By the term "tuned telephone," is meant a telephone which is substantially free from reactance for the frequency employed and whose diaphragm has a natural period of vibration, for its fundamental, which is the same as that of the current.

The resistance of that portion of the bridge wire between the center

of the bridge and the position of the sliding contact will be denoted by  $\Delta R_B$ . This resistance is just sufficient to cause an audible sound in the telephone and the current flowing through the telephone under these conditions will be its "audibility current,"  $I_T$ .

**3. The Distribution of the Current in the Bridge Network.**—With the aid of Kirchhoff's laws, the following expression for the total current  $I$  through the bridge may be readily obtained in the same manner as for direct currents:<sup>3</sup>

$$I = \frac{I_T}{2 \Delta R_B} \left[ \frac{(R_B/2 + Z)^2 + 2R_T(R_B/2 + Z)}{Z} \right] \quad (1)$$

where the impedance  $Z$  is, of course, a complex quantity, which in the present instance is expressed by the equation

$$Z = \frac{-jR}{2\pi fCR - j} \quad (2)$$

If we substitute this expression into Equation 1 and separate the resulting expression into its real and imaginary parts, we find for the real part

$$I = \frac{I_T}{2 \Delta R_B R} \sqrt{\left[ \frac{1/4 R_B^2 + R R_B + \frac{R^2}{\frac{f^2 k^2}{324 \cdot 10^{22} \bar{L}^2} + 1} + 2R_T R + R_T R_B}{\frac{f^2 k^2}{324 \cdot 10^{22} \bar{L}^2} + 1} \right]^2 + \left[ \frac{1/4 R_B^2 + R_T R_B - \frac{R^2}{\frac{f^2 k^2}{324 \cdot 10^{22} \bar{L}^2} + 1}}{\frac{f^2 k^2}{324 \cdot 10^{22} \bar{L}^2} + 1} \right]^2} \quad (3)$$

where  $k$  is the dielectric constant of the liquid in the cell and  $\bar{L}$  is its specific conductance.

An inspection of this equation shows that for good conductors it reduces to

$$I = \frac{I_T}{2 \Delta R_B R} \left[ \left( \frac{R_B}{2} + R \right)^2 + 2R_T \left( \frac{R_B}{2} + R \right) \right]. \quad (4)$$

As the value of  $\bar{L}$  decreases and the resistance of the cell increases, however, the two expressions differ from each other more and more. If we put  $\bar{L} = 10^{-7}$  and  $R = 10^5$ , then if  $f$  is not greater than 1000 cycles and  $k$  is not greater than 80, Equation 3 does not differ from Equation 4 by more than 10% of the value of  $I$ . Within this degree of accuracy, therefore, we may use Equation 4 in place of Equation 3 as long as we are dealing with solutions whose specific conductance does not fall below  $10^{-7}$  reciprocal ohms.

It will be noticed that this range includes all aqueous solutions down to and including the best "conductivity water" that can be prepared and handled in contact with the atmosphere, even under the most favorable

<sup>3</sup> Maxwell, *Electricity and Magnetism*, 1, 477.

conditions.<sup>4</sup> For the large majority of investigators engaged in conductivity measurements with solutions of electrolytes the above range is sufficiently ample to include all the cases which they meet with in practice. For this reason it seems best in the interest of simplicity to restrict the present discussion to liquids whose specific conductances fall within the range mentioned, since the relations obtained will be much simpler if we can employ Equation 4 instead of the more general and more complex Equation 3. Moreover the applications of the general equation to cases which lie without the above range are of more interest in connection with measurements of dielectric constants than in connection with conductance measurements because, when the specific conductance of the material begins to drop below  $10^{-8}$ , it becomes possible in most instances to use the direct current and galvanometer for the conductance measurements and under these conditions Equation 4, of course, becomes rigorously exact for all cases. The author hopes at some future time to discuss the subject of dielectric constant measurements in the light of Equation 3, particularly with reference to the problem of determining the dielectric constant of salt solutions, a problem which was taken up experimentally in this laboratory last year but which will now have to be dropped.

**4. The Theory of Cell Design.**—In the process of determining the correct bridge setting, the portion of the bridge-wire over which the "minimum" extends will evidently have a resistance equal to  $2\Delta R_B$  ohms (see Fig. 1). Within this range *no sound* will be heard in the telephone. The uncertainty in judging the exact center of this minimum will evidently be larger the larger  $2\Delta R_B$  is, but with properly designed apparatus this uncertainty should never amount to as much as one-fourth of the total range, that is, to as much as  $\frac{1}{2}\Delta R_B$ , and this would produce an error of  $p\%$  in the resistance of the cell. We shall, therefore, be conservative, if we write

$$2\Delta R_B = \frac{pR_B}{100} \quad (5)$$

where  $p$  is the allowable percentage error from the bridge setting.

The relation between the Current  $I_A$  and the Current  $I$  (see Fig. 1) is evidently

$$\frac{I_A}{I} = \frac{R_B}{2R + R_B} \quad (6)$$

If we combine Equations 4, 5 and 6 we have

$$I_A = \frac{50I_T(R_B/2 + R + 2R_T)}{pR} \quad (7)$$

For the purposes of the present discussion we shall assume that the

<sup>4</sup> Cf. J. E. Bell, Univ. of Ill. Thesis, 1913, p. 16.

conductivity cell contains two parallel electrodes of approximately equal areas. These electrodes will be  $l$  centimeters apart and the area of the *uniform* cross-section of the solution between them will be  $A$  square centimeters. The electrodes may be either two metal disks closing the ends of a cylindrical tube containing the solution, or they may be two sufficiently large coaxial cylinders. The area of each electrode must be substantially equal to or larger than the effective area of the cross-section of the solution between them. The heat capacity of the solution between the electrodes will be  $Alds$ , where  $d$  is the density of the solution and  $s$  its specific heat capacity.

If during the operation of determining the bridge setting the temperature of the solution between the electrodes rises  $\Delta T^\circ$  because of the current  $I_A$  passing through the cell, the energy thus liberated will be  $Alds\Delta T \cdot 4.2$  Joules. Equating this to the electrical energy, we have

$$Alds\Delta T \cdot 4.2 = I_A^2 \frac{lt}{A\bar{L}} \quad (8)$$

where  $\bar{L}$  is the specific conductance of the solution and  $t$  is the time required to obtain the final correct bridge setting.

If  $\alpha$  is the temperature coefficient of the conductance of the solution in the cell, a rise of  $\Delta T^\circ$  in the temperature during the measurement will produce a percentage error

$$p_T = 100\alpha\Delta T. \quad (9)$$

Now there is no particular advantage to be gained by attempting to make the error from this source less than that arising from the uncertainty in the bridge setting. We shall, therefore, equate these two sources of error.

$$p_T = p. \quad (10)$$

We can now write

$$\Delta T = \frac{p}{100\alpha}. \quad (11)$$

and Equation 8 becomes

$$\frac{Alds p \cdot 4.2}{100\alpha} = I_A^2 \frac{lt}{A\bar{L}}. \quad (12)$$

Combining this with Equation 7 so as to eliminate  $I_A$  and solving for  $A$ , we have the condition

$$A \geq \frac{50 I_T [R_B/2 + R + 2R_T] t^{1/2}}{R \bar{L}^{1/2} \sqrt{\frac{p^3 ds}{\sim 0.042}}} \quad (13)$$

If we put

$$R = \frac{l}{A\bar{L}} \quad (14)$$

in Expression 13 and again solve for  $A$ , we obtain the important condition

$$A^2 \geq \frac{6 \cdot 10^4 I_T^2 l^2 t}{\bar{L} [l \sqrt{p^3 ds/\alpha} - 120 I_T \sqrt{t \bar{L}} (R_B + 4R_T)]^2}. \quad (15)$$

This relation gives the minimum allowable value for the cross-section of the cell, if the two sources of error indicated are not to exceed  $p\%$  each. By solving this equation for  $l$ , we obtain a similar relation giving the maximum allowable value for the distance between the electrodes for the same condition.

For many purposes, however, a more convenient expression is obtained by solving the equation for  $\bar{L}$  giving us

$$\bar{L} = \frac{l^2 p^3 ds/\alpha}{6 \cdot 10^4 I_T^2 t (R_B + 4R_T)^2} \left[ 1 \pm \sqrt{1 - \frac{1.2 \cdot 10^5 I_T^2 t (R_B + 4R_T)}{A l p^3 ds/\alpha}} \right]^2. \quad (16)$$

This equation gives two values for  $\bar{L}$ . These two values represent the limits between which it is safe to use the cell in question if the two sources of error indicated are not to exceed  $p\%$  each. These two limiting values of  $\bar{L}$  determine what we shall call the *ultimate range* of the cell. No conductivity cell should ever be used for solutions with specific conductances which do not lie within the *ultimate range* of the cell as defined by the above equation.

In determining the actual *working range* of a given cell, however, another factor must also be taken into account, and that is the range of resistances within which it is practicable or desirable to make measurements. If  $R_{\max.}$  is the highest and  $R_{\min.}$  the lowest resistance which it is desirable to undertake to measure, then in addition to the above condition, the following must also be fulfilled:

$$\frac{l}{AR_{\max.}} > \bar{L} > \frac{l}{AR_{\min.}} \quad (17)$$

Before proceeding further with the discussion of the use of the principles thus far derived, it will be convenient to simplify the nomenclature somewhat. We shall introduce the following abbreviations:

$$p^3 ds/\alpha = a \quad (18)$$

$$I_T^2 t = b \quad (19)$$

and

$$R_B + 4R_T = c \quad (20)$$

Furthermore, if  $\bar{L}_1$  and  $\bar{L}_2$ , respectively, represent the upper and lower limits of the range of the cell, then the *range ratio*  $r$  will be defined by the expressions

$$\frac{\bar{L}_1}{\bar{L}_2} = r \text{ and } r \leq \frac{R_{\max.}}{R_{\min.}}. \quad (21)$$

Equation 16 can now be written

$$\frac{\bar{r}}{6.10^4 bc^2} = \frac{l^2 a}{\left[ 1 \pm \sqrt{1 - \frac{1.2 \cdot 10^5 bc}{Ala}} \right]^2} \quad (22)$$

and Expression 13 may be written

$$A \geq \frac{122 \cdot b^{\frac{1}{2}} (2R_{\max.} + c)}{R_{\max.} \bar{L}_2^{\frac{1}{2}} a^{\frac{1}{2}}} \quad (23)$$

where  $R_{\max.}$  is the resistance of the cell when filled with a liquid having the specific conductance  $\bar{L}_2$ .

If  $R_{\max.}$  is more than ten times  $c$ , which will practically always be the case when  $R_{\max.}$  is not less than 10,000 ohms,  $c$  may be neglected in comparison with  $R_{\max.}$  and the above expression reduces to the simple form

$$A \geq \frac{244 \cdot b^{\frac{1}{2}}}{\bar{L}_2^{\frac{1}{2}} a^{\frac{1}{2}}} \quad (24)$$

or in words, the minimum allowable value for the cross-section of the cell is determined by the audibility current of the telephone, the specific conductance of the liquid having the maximum desired resistance in the cell, the density, heat capacity and conductance temperature-coefficient of this liquid, and the percentage accuracy demanded in the measurement. It does not, however, depend upon the distance between the electrodes, that distance being fixed (after the value of  $A$  has been decided upon) by means of the equation

$$l = \bar{L}_2 A R_{\max.} \quad (25)$$

Expressions 23 and 25 together, therefore, fix a minimum volume for the cell. There is, however, another relationship involving the product  $Al$  which must also be satisfied. That is the relationship involved in Expression 22 which we will now proceed to examine more closely.

*The Volume Factor of a Conductivity Cell.*—From Equations 19 and 20 we obtain

$$\frac{\bar{L}_1}{\bar{L}_2} = r = \frac{\left[ 1 + \sqrt{1 - \frac{1.2 \cdot 10^5 bc}{Ala}} \right]^2}{\left[ 1 - \sqrt{1 - \frac{1.2 \cdot 10^5 bc}{Ala}} \right]} \quad (26)$$

and if we solve this equation for the product  $Al$ , we obtain the following expression which determines the minimum allowable value for what we shall call the *volume factor* of our cell.

$$Al \geq \frac{(r^{\frac{1}{2}} + 1)^2 \cdot 1.2 \cdot 10^5 bc}{4r^{\frac{1}{2}} a} \quad (27)$$

Since it will not ordinarily be desirable to restrict the range ratio of a cell to a value less than  $10^3$ , Expression 27 can for most purposes be written

$$Al \geq \frac{3 \cdot 10^4 \cdot bcr^{1/2}}{a} \text{ approx.} \quad (28)$$

It will be noticed that for a series of cells having the same range ratios, the minimum allowable value for the volume factor of the cells is the same for all the cells independent of their particular ranges.

Now if a cell is designed in accordance with the principles set forth in Expressions 23 and 25 a minimum value for its volume factor is also determined thereby. It is necessary, therefore, to ascertain whether this minimum is greater or less than the one fixed by Expression 27. If it is always greater, then Expression 27 need not be considered in designing cells, for the condition which it lays down would always be met if Expressions 23 and 25 are satisfied. We shall proceed to discover the conditions under which the minimum volume factor given by Expressions 23 and 25 shall always be greater than the value demanded by Expression 27.

We proceed as follows: From Expressions 23 and 25 we find

$$Al \geq \frac{1.5 \cdot 10^4 \cdot b(2R_{\max.} + c)^2}{R_{\max.} a} \quad (29)$$

The condition desired is, therefore, expressed by the relation

$$\frac{1.5 \cdot 10^4 \cdot b(2R_{\max.} + c)^2}{R_{\max.} a} \geq \frac{(r^{1/2} + 1)^2 3 \cdot 10^4 bc}{ar^{1/2}} \quad (30)$$

Putting  $R_{\max.} = rR_{\min.}$  in this relation and solving it for  $c$ , we find the two alternative conditions

$$c \geq R_{\min.} [r^{1/2} (r + 1) + \sqrt{r(r + 1)^2 - 4r^2}] \quad (31)$$

or

$$c \leq R_{\min.} [r^{1/2} (r + 1) - \sqrt{r(r + 1)^2 - 4r^2}]. \quad (32)$$

Of these two conditions the first one may ordinarily be disregarded because it usually gives values for  $c$  which are very much greater than any which would be met with in practice. Expression 32 then describes the condition which must be fulfilled if Expression 29 is to take precedence over Expression 27 in determining the dimensions of a conductivity cell. In nearly all cases which will be met with in actual practice, it will be found that the above condition will be fulfilled and that hence no attention need be paid to Expression 27 in designing conductivity cells. In a few very special cases, however, account must be taken both of Equation 31 and Equation 27. As an illustration of such an instance we shall at this point consider briefly the problem of designing a conductivity cell which shall have a minimum volume factor.

*To Design a Conductivity Cell Having a Minimum Volume Factor.—*

It is sometimes necessary to determine the conductivity of a liquid of which only a very small quantity is available. This is the case in studies of the conductivity of the sap of plants, for example. In such cases it



is important to employ a cell which requires a minimum amount of liquid to fill it.

To take a concrete example suppose the specific conductances of different samples of a certain group of plant saps lie within the limits  $\bar{L}_1$  and  $\bar{L}_2$  and that it is desired to measure the specific conductances of these saps with an accuracy of  $p\%$ . Let us suppose further that

$$r = \frac{\bar{L}_1}{\bar{L}_2} \gg 10. \quad (33)$$

Applying the criteria in Expressions 31 and 32 we find the two *alternative* conditions

$$6.3 R_{\min.} \geq c \geq 63 R_{\min.} \quad (34)$$

If, as would normally be the case,  $100 \ll R_{\min.} \ll 20$ , we would usually find that neither of these conditions was satisfied. This would mean that the volume factor of our cell would be determined by Equation 27 which in this case would become

$$Al \geq 1.65 \cdot 10^5 bc/a. \quad (35)$$

After having determined the minimum volume factor from this relation, the values of  $A$  and  $l$  would then be separately obtained by combining with the equation

$$l = A\bar{L}_1 R_{\min.} \quad (36)$$

We shall complete this discussion in the numerical form after considering some typical numerical values of  $a$ ,  $b$  and  $c$  (see Sec. 7 below).

**5. The Adjustment of the Total Current through the Bridge for a Conductance Measurement.**—In the theory of cell design presented above, one of the principal features is the entire elimination of any appreciable heating of the cell during the measurement. It is obvious, however, that *any* cell *could be* appreciably heated if a large enough current is employed for the measurement. The regulation of the current through the bridge is, therefore, an important element in the use of the cells.

It will be noticed, however, that the value of  $I$ , the total current through the bridge, does not appear in any of the final equations which control the cell design. Stated in words this means that a knowledge of the actual value of the current through the bridge is unnecessary either for the purpose of designing the cells or for using them afterwards. By looking back to Sec. 4 it will be noticed that at the beginning of the development of our theory a definite restriction was as a matter of fact placed upon the value of  $I$ . This restriction is involved in writing Equation 5 and the rule for adjusting the current through the bridge for the final measurement may, therefore be formulated as follows: Increase the current from the generator until the following condition is fulfilled:

$$\Delta R_B \leq \frac{pR_B}{200} \text{ approx.} \quad (37)$$

where  $p$  is the maximum percentage accuracy which the cell is designed to give with the telephone employed with it, and  $R_B$  is the approximate resistance of the bridge. Or stated in another way,  $p$  may have any desired value, not less than  $100\alpha\Delta T'$ , provided the cell is not used outside of the conductance range fixed by Equation 22.

**6. Summary.**—The results of the foregoing discussion may be summed up as follows:

Given the problem, *To construct a conductivity cell with a range ratio*  
 $r = \frac{R_{\max.}}{R_{\min.}} = \frac{\bar{L}_1}{\bar{L}_2}$ , *where*  $R_{\min.}$  *is the resistance of the cell when filled with*  
*a liquid of specific conductance*  $\bar{L}_1$  *and*  $R_{\max.}$  *is the resistance of the cell when*  
*filled with a liquid of specific conductance*  $\bar{L}_2$ .

The answer is: 1. Determine the minimum allowable value for the area of the cross-section between the electrodes with the aid of Expression 24; 2. Choose any convenient value larger than this; and then, 3. Determine the distance between the electrodes by means of Equation 25.

Stated in other words, *The area of the cross-section between the electrodes of a conductivity cell must not be less than a certain minimum value which is completely fixed and determined by the audibility current of the telephone, the time required to make the bridge setting, the lowest specific conductance which it is desired to include within the range of the cell and the percentage accuracy demanded in the measurements.*

This practically means that conductance cells should be designed to fit the telephone which is to be employed with them. The audibility current of the telephone is the chief controlling factor and every investigator making conductance measurements should determine for himself the audibility current of his telephone because the value of this important quantity is a function both of the construction of the telephone and of the observer's ear. The audibility current can be conveniently determined by methods which will be described in the second paper of this series, which will appear very shortly.

**7. Numerical Values of the Variables which Control the Cell Design.**—Before proceeding to the discussion of the application of the above principles to concrete cases, it will be necessary to assign appropriate numerical values to the variables involved. The factors governing the selection of these values will now be considered.

*The Resistance of the Slide-wire.*—The theoretical and practical principles which govern the selection and arrangement of the resistance or resistances which make up that portion of the Wheatstone bridge included between the points  $A$  and  $B$  of Fig. 1, will be considered in detail in a later paper. For our present purposes, it will be sufficient to note that according to Equation 1, the best value for  $R_B$  is given by the equation

$$R_B = 2\sqrt{Z(Z + 2R_T)} \quad (38)$$

or for aqueous solutions

$$R_B = 2\sqrt{R(R + 2R_T)}. \quad (39)$$

As a matter of fact, except for very small or very large values of  $R$  it is not necessary to pay much attention to fulfilling the condition expressed by this equation because sufficient accuracy can be obtained with a single bridge wire over a wide range of resistances. One of the slide-wire bridges in extensive use at the present time for measuring the conductances of electrolytes has a slide-wire which with its extension coils has a total resistance in the neighborhood of 250 ohms. This is an appropriate value for general use and in the following illustrative calculations we shall accordingly assume

$$R_B = 250 \text{ ohms.} \quad (40)$$

*The Resistance and Sensitivity of the Telephone.*—Theoretically, other things being equal, a high-resistance telephone should be employed for measuring high resistances and a low-resistance telephone for low resistances but practically the sensitivity is at present the only determining factor in the choice of a telephone. A very satisfactory telephone on the market at present has an audibility current<sup>5</sup> not greater than  $2 \cdot 10^{-9}$  ampere and a resistance of 150 ohms. We shall assume these values in the following calculations and write

$$J_T = 2 \cdot 10^{-9} \text{ ampere} \quad (41)$$

and

$$R_T = 150 \text{ ohms.} \quad (42)$$

*Density and Heat Capacity of the Solution.*—In the following calculations we shall assume

$$ds = 1. \quad (43)$$

This assumption will not be far from the truth in the case of aqueous solutions of electrolytes and in cases where this assumption is not sufficiently exact the necessary modifications of the equations will be obvious.

*Time Required to Obtain the Bridge Setting.*—This factor will vary with the observer, the apparatus he is using and a variety of conditions prevailing at the time of observation. Experiments in this laboratory have shown that a trained observer working in quiet surroundings with good apparatus can, if necessary, make the final bridge setting in about five seconds, even when measuring resistances as high as 50,000 ohms. In designing cells, however, it is better where possible to allow a somewhat longer time than this. We have found that a period of 10 seconds is usually ample to make a leisurely bridge setting if good apparatus is employed. We shall accordingly write

$$t = 10 \text{ seconds.} \quad (44)$$

For any given cell the maximum allowable value for  $t$  can be calculated

<sup>5</sup> Determined for the writer's ear.

from Equation 15. It is well to know this maximum value for  $t$  before measurements are begun with a new cell. Moreover if for any reason an observer wishes a longer time than 10 seconds, the design of the cell can, of course, be made to meet his condition. The following numerical calculations are given only as illustrations.

*Maximum and Minimum Values for the Resistance of the Cell.*—To a considerable extent the values of  $R_{\max.}$  and  $R_{\min.}$  may be chosen arbitrarily and the dimensions of the cell made to correspond with the values chosen. In the following illustrative calculations we shall assume

$$R_{\min.} = 100 \text{ ohms.} \quad (45)$$

This value is sufficiently large to make the elimination of errors due to lead resistances and contact resistances comparatively easy. Moreover it will always be practicable to construct the cell to meet this condition even for solutions of the highest specific conductance. For  $R_{\max.}$  we shall employ the value 10,000 ohms as long the dimensions of the cell will conveniently permit, but for cells to be used for poorly conducting liquids we shall include the case  $R_{\max.} = 100,000$  ohms.

*Temperature Coefficient of Conductivity.*—In the following calculations we shall write, for salt solutions,

$$\alpha = 0.02 \quad (46)$$

as an average value. In the case of conductivity water, however, we shall employ  $\alpha = 0.05$ .

*Percentage Accuracy Desired in the Measurement.*—With the apparatus now available for measuring the conductivity of electrolytes, the degree of precision attainable in the measurement is entirely determined and limited by the magnitude of the unavoidable variation of the temperature of the bath containing the cell. All other sources of variable error are now entirely negligible in comparison with this one. If therefore,  $\Delta T'$  represents the temperature range covered by the fluctuations of the "constant temperature" bath containing the cell, it is obvious that the maximum attainable percentage accuracy, that is, the minimum percentage error in the conductivity measurement is given by the equation

$$p_{\min.} = 100\alpha\Delta T' \quad (47)$$

Now there will obviously be no advantage in making the other sources of error much smaller than this one. We shall, therefore write

$$p = p_T = \frac{1}{2}p_{\min.} = 50\alpha\Delta T'. \quad (48)$$

For solutions of electrolytes where  $\alpha = 0.02$  and  $\Delta T'$  is taken as  $0.001^\circ$  this becomes

$$p = \Delta T' = 10^{-3} \quad (49)$$

and for conductivity water where  $\alpha = 0.05$ , it becomes

$$p = \text{approximately } 3 \cdot 10^{-3} \quad (50)$$

which are the values which we shall employ in the following calculations.

It will be noted that the choice of the above values imposes the condition that the rise in the temperature of the solution produced by the current which passes through it during the measurement shall not exceed  $0.0005^\circ$ . This requirement is evidently sufficiently exacting for all practical purposes. A more exacting requirement in this respect would be useless unless the fluctuations of the constant temperature bath could be made considerably less than  $0.001^\circ$ .

Using the above numerical values we have

$$a = p^3 ds/\alpha = 5 \cdot 10^{-8} \text{ (or for conductivity water = } 54 \cdot 10^{-8} \text{) calories per cc.} \quad (51)$$

$$b = I_T^2 t = 4 \cdot 10^{-17} \text{ coulomb-amperes.} \quad (52)$$

$$c = R_B + 4R_T = 850 \text{ ohms} \quad (53)$$

and the set of expressions derived above may be written:

Equation 22

$$\bar{L} = 2.9 \cdot 10^{-2} l^2 \left[ 1 \pm \sqrt{1 - \frac{8.2 \cdot 10^{-2}}{Al}} \right]^2 \quad (54)$$

Expression 24

$$A \geq \frac{6.9 \cdot 10^{-3}}{\bar{L}^{1/2}} \quad (55)$$

or for conductivity water ( $\bar{L} = 10^{-7}$ )

$$A \geq 7.0 \quad (56)$$

Expression 25

$$Al \geq \frac{(r^{1/2} + 1)^2}{r^{1/2}} \cdot 2 \cdot 10^{-2} \quad (57)$$

or for  $r = 10^3$

$$Al \geq 0.665 \quad (58)$$

Furthermore, if we apply the test imposed by Expression 32 using  $r = 10^3$ , we find the condition

$$c \leq 60R_{\min.} \quad (59)$$

a condition which is evidently fulfilled. We must, therefore, employ Expression 24, or in this instance 55, in determining the minimum value for  $A$ . For this purpose it will be most convenient to construct a graph of this equation. Such a graph is shown in Fig. 2, Curve A. The ordinates represent values of  $A$  in square centimeters and the abscissae, corresponding values of  $\bar{L}_2$  expressed as powers of ten. The point corresponding to  $\bar{L}_2 = 10^{-7}$  is that given by Expression 56. The corresponding curve for  $D$ , the diameter of the cross-section of the cell, is shown on the same diagram.

This diagram can also be employed in designing cells for use with a telephone for which  $I_T > 6 \cdot 10^{-8}$ , if  $p < 10^{-2}$  or for which  $I_T > 2 \cdot 10^{-8}$ , if  $p < 10^{-1}$ .

We shall now proceed to illustrate the use of this diagram in designing a set of conductivity cells to cover the whole range of specific conductances between 1 and  $10^{-7}$  reciprocal ohms.

### 8. Types of Conductivity Cells.

*General Features.*—Every conductivity cell designed for accurate work should fulfill the following obvious conditions:

1. It should be so formed that the operation of filling it with the solution to be measured and its subsequent use exposes the solution as little as possible to the action of the atmosphere.

2. The material of which it is constructed should not contaminate the solutions to be used in it.

3. The electrodes should be of such size and weight that when fixed firmly in one position the cell constant will not change with use, and the electrodes should be so placed that the cell constant does not depend upon the height to which the cell is filled. The electrode stems

should be as short as the conditions of manufacture and of filling and washing the cell will permit.

A cell constructed in the form of a pipet<sup>6</sup> probably fulfills the first condition most satisfactorily. Types<sup>7</sup> of pipet cells which have been in use in this laboratory for a number of years are shown in Figs. 3, 4, 5 and 6.

*Type A.*—This type is for use with conductivity water and very dilute solutions. For use with conductivity water the electrodes may be placed vertically since they are so close together that no appreciable number of lines of flow will reach the surface of the liquid, if the precaution is taken to fill the cell up to the level of the arrows A and D. The right-angled

<sup>6</sup> The writer is not aware of the origin of the pipet form for a conductivity cell. Such a cell is pictured and mentioned in Ostwald-Luther's *Handbuch*, 1902 Ed., and a cell of this form was constructed in this country in 1907 by Kraus (THIS JOURNAL, 31, 732 (1909)).

<sup>7</sup> In the case of Type A the figure is drawn so as to exhibit a form of construction which will permit a minimum electrode stem length, which may be desired in some cases for the reasons explained in Sec. 13. If this is not required the body of the cell is most easily made in the globular form shown in THIS JOURNAL, 35, 752 (1913), Fig. 1.

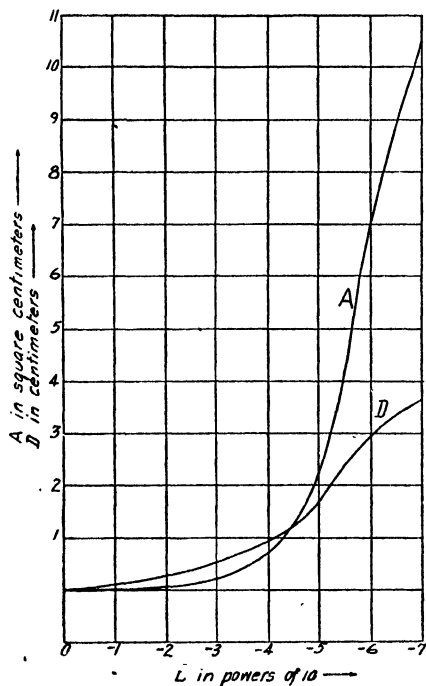


Fig. 2.

turn in the tube above the electrodes is an additional precaution against the escape of lines of flow to the surface of the liquid. The electrodes are constructed of the purest platinum alloyed with enough iridium to render them stiff. Each electrode is in the shape of a disk about 0.15 mm. thick and supported at the center by a rod of the same material about 1.5 mm. in diameter. The end of this rod may be slightly flanged before it is welded on to the disk in order to increase the strength of the joint and insure perfect rigidity after the electrode has been sealed into position. The inside surfaces of both electrodes should be roughened with a sand blast.

For use with dilute solutions the electrodes are lightly platinized and are preferably placed in a horizontal position (Fig. 4).

*Type B.*—This type is for use with moderately good conductors. The electrode specifications are the same as for Type A, except that a lighter weight platinum may be employed. The electrodes should be covered with a sufficiently heavy coating of platinum black to insure the elimination of polarization (see Sec. 14 below) but the coating should not be any heavier than necessary to accomplish this purpose.

*Type C.*—This type is for use with good conductors. The electrode specifications are the same as for Type A except that the electrodes may be made in the shape of a bowl as shown in the figure and the lower electrode should have a circular perforation at least 2 mm. in diameter near the center of the bottom. The diameter of the bowl may be about 5 centimeters and the depth about 7 millimeters. Both electrodes should be heavily platinized. The electrodes may be placed with their convex sides towards each other as shown in the figure, or they may be placed with their concave sides facing each other. The second arrangement makes a somewhat more efficient use of the electrode surface but it is necessary to guard carefully against the inclosure of a bubble of air underneath the upper electrode in this arrangement. A bubble of air below the lower electrode in the arrangement shown in the figure will do much less harm.

**9. A Series of Cells Covering the Complete Conductance Range for Aqueous Solutions.**—*Cell No. 1. For Conductivity Water.*—This cell will have nonplatinized electrodes and will be employed for solutions with specific conductances ranging from  $1.6 \cdot 10^{-7}$  reciprocal ohms up to a value which will be determined by the appearance of a poor minimum due to the influence of polarization. From Fig. 2 we find  $A = 10.4$  square centimeters. For circular electrodes this would correspond to a diameter of 3.65 centimeters. Suppose we choose 4 centimeters as the maximum diameter which we wish to employ for this type of electrode. This would mean an area of 12.6 square centimeters. Suppose moreover that it is undesirable to place these electrodes nearer together than 2 millimeters. If we put  $R_{\max.} = 10^5$  ohms we find from Equation 25,  $\bar{L}_2 = 1.6 \cdot 10^{-7}$ .

In other words such a cell could be used for conductivity water down to a specific conductance of  $1.6 \cdot 10^{-7}$  reciprocal ohms. This is practically the purest water which can be prepared in contact with the atmosphere<sup>4</sup> and hence the above cell would fill all requirements for conductivity water which is to be handled in contact with the atmosphere. The cell would be of Type A, Fig. 3.

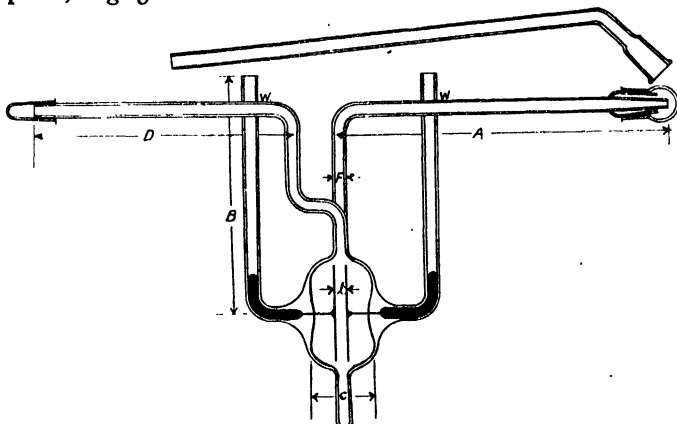


Fig. 3.—Water cell. Type A

For measuring conductivities less than  $1.6 \cdot 10^{-7}$  it is convenient to use electrodes in the form of two coaxial cylinders.<sup>8</sup> A pair of such electrodes about 4 centimeters long, .4 centimeters across and 3 millimeters apart could be employed for specific conductances down to  $0.6 \cdot 10^{-7}$  without the resistance rising above  $10^5$  ohms. A study of the conductivities of dilute solutions in water having an initial conductivity of  $0.6 \cdot 10^{-7}$  reciprocal ohms at  $18^\circ$  is now in progress in this laboratory.

*Cell No. 2. For Dilute Solutions.*—This cell will have lightly platinized electrodes and will be designed to cover the range between  $10^{-6}$  and  $10^{-4}$  reciprocal ohms. From Fig. 2 we find  $D \geq 3$  centimeters. We shall choose the value 4 centimeters for the diameter of the electrodes and of the cross-section of the cell. For the distance between the electrodes we shall take 3 millimeters. The cell will be of the same type as No. 1 and when filled with a liquid of specific conductance  $10^{-6}$  reciprocal ohms will have a resistance of 24,000 ohms.

It will be noticed that the ranges of Cells 1 and 2 overlap to a considerable extent. This is desirable in the case of these cells because the upper limit of Cell No. 1 will be determined by the appearance of polarization influences and recourse will then have to be had to Cell No. 2. Needless to say it is advantageous to employ Cell No. 1 as long as possible because contamination of the solution by materials adsorbed by platinum

<sup>8</sup> A form of electrode originated by Pfeiffer [*Wied. Ann.*, 25, 232 (1885)].



Cell No. 3. Range  $10^{-4}$  to  $10^{-2}$ .—This cell will have well platinized electrodes. The diameter of the cross-section of the cell will be 1.5 centimeters and the distance between the electrodes 1.8 centimeters. It will be noticed that these dimensions fulfill the conditions shown by the diagram and give the cell a resistance of  $10^4$  ohms at the lower limit of the above range. The cell will be of Type B, Fig. 5.

*Discussion.*—These four cells will cover the total conductance range between 1 and  $10^{-7}$  reciprocal ohms. It is obvious that a greater number of cells could be employed if desired and that considerable variation in the dimensions is possible within the limits set by the diagram. It will be noted that with the above set of cells it is not necessary to employ a resistance greater than 10,000 ohms until the specific conductance of the

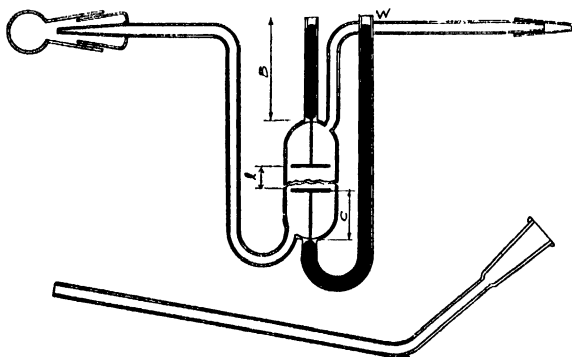


Fig. 5. Type B

liquid falls below  $1.6 \cdot 10^{-6}$  reciprocal ohms. The whole range could be covered with three cells by taking  $R_{\max.} = 10^5$  for each cell. Where it can be done conveniently, however, it is desirable to keep the value of  $R_{\max.}$  not greater than  $10^4$  ohms since there is then less trouble in obtaining a sufficiently close balance of the capacities in the two arms



many cases less sensitive than this, the corresponding values of  $Al$  would be 2.8 cc. and 0.003 cc., respectively.

Evidently these values are so low that there is practically no danger in falling below them in constructing cells for small quantities of liquids unless a larger range ratio than 10 is demanded for the cell. They are so low in fact that the total volume of the cell would in most cases be

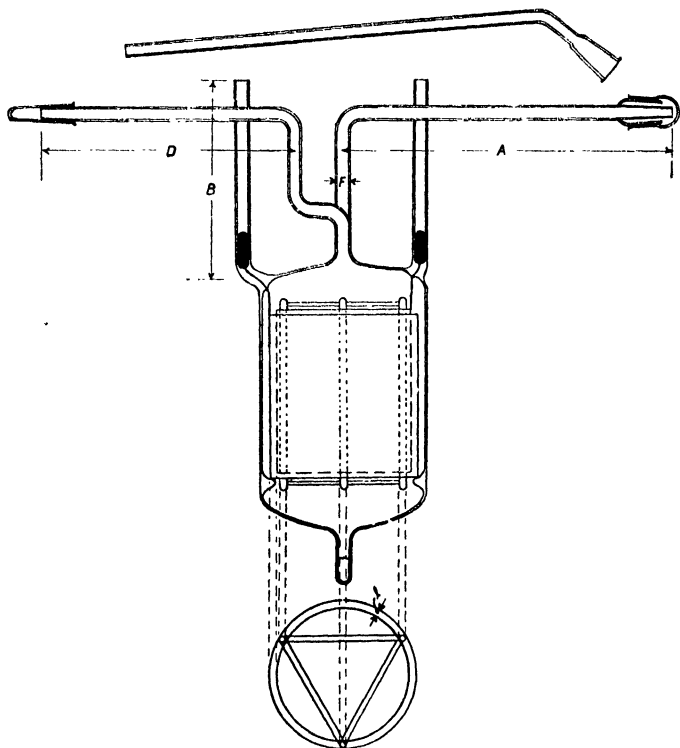


Fig. 7.—Scale: 1 inch = 3 inches.  $l = 0.2$  cm.

practically determined by the space necessary to inclose electrodes of sufficient size to eliminate polarization, unless the method described in Sec. 14b were employed for this purpose.

**11. Connecting the Cell to the Bridge.**—In accurate work the conductivity cell should never be directly connected to the lead wires coming from the bridge but instead a pair of mercury cups *dipping into the bath containing the cell* should always be employed as an intermediary, as illustrated in Fig. 8. The reason for this is, of course, to prevent the exchange of heat between the electrodes and the room, along the connecting wires. For the same reason the distance  $B$  in Figs. 3-7 should be long enough to permit the submersion of all of the body and a good part of the connecting tubes of the cell, below the surface of the bath. Insulated

wires with amalgamated ends are used for bridging across between the cell and the intermediate mercury cups as shown in Fig. 8.

Twisted lamp cord No. 11 is, in practically all cases, of ample size<sup>9</sup> for connecting the intermediate mercury cups with the bridge and if the

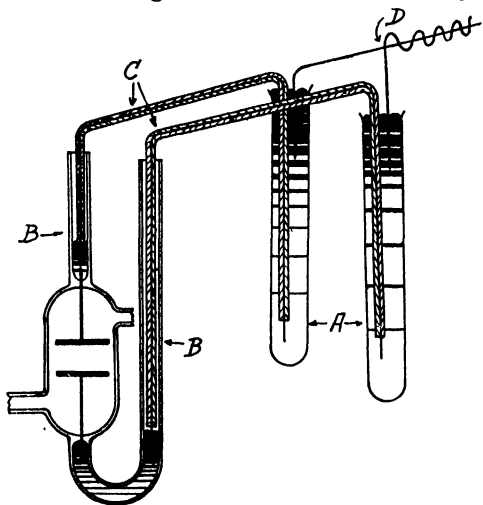


Fig. 8.

same length of this cord is employed in connecting the bridge with the resistance box, it will never be necessary to determine or apply any correction for lead resistance, as long as the distance between the bridge setting and the center of the bridge is not greater than  $n/10000$  of the total bridge length,  $n$  being given by the expression

$$n = \frac{5000R_{pL}}{R_{pL} + 200R_L} \quad (61)$$

where  $R_L$  is the resistance of each pair of leads.

The resistance of the wires used to bridge across from the cell to the intermediate mercury cups as well as the resistance of the mercury and of the platinum stems of the electrodes are counted as part of the total lead resistance,  $R_L$ , of the cell.

**12. The Temperature Coefficient of the "Cell Constant" of a Conductivity Cell.**—As is well known, the Cell Constant of a conductivity cell changes with the temperature. The rapidity with which it changes, however, varies with the manner in which the cell is constructed and depends upon the nature of the materials which compose it. The nature of this dependence can be deduced as follows:

*Cells of Types A and B.*—For simplicity let us assume that the lines of flow are all perpendicular to the surface of the electrode, that is, we shall neglect the "edge effect," which will be smaller the more tightly the electrodes fit the cell and the smaller  $l$  is. For the Cell Constant of such a cell we will then have

<sup>9</sup> This size of lead wire is calculated as follows: From Equation 61 we find our limiting condition

$$\underline{R} \geq \frac{(5000 - n)R_{\min}p_L}{400nh}$$

where  $\underline{R}$  is the resistance of the wire in ohms per foot, and  $h$  is the distance between the cell and the bridge. Putting  $n = 200$ ,  $R_{\min} = 100$ ,  $h = 2$  ft. and  $p_L = 5 \cdot 10^{-4}$ , we find  $\underline{R} = 15 \cdot 10^{-4}$  ohms per foot = about No. 11 B. & S. copper wire. Similarly for  $h = 1$  ft. and  $p_L = 5 \cdot 10^{-3}$  we find  $\underline{R} = 3 \cdot 10^{-2}$  ohms per foot = about No. 25 B. & S. copper wire, etc., for any conditions which may be demanded.

$$K = \frac{l}{A} \quad (62)$$

and therefore,

$$A \frac{dK}{dt} = \frac{dl}{dt} - \frac{l}{A} \frac{dA}{dt} \quad (63)$$

For the two derivatives of  $l$  and  $A$  we have

$$\frac{dl}{dt} = \beta(l + s) - \gamma s \quad (64)$$

and

$$\frac{dA}{dt} = 2\gamma A \quad (65)$$

respectively, where  $s$  is the total length of the two platinum rods which support the electrodes,  $\gamma$  is the linear coefficient of expansion of platinum and  $\beta$  the coefficient of linear expansion of the material of which the cell is constructed. Combining these two expressions with Equations 62 and 63, we have the desired expression for the temperature coefficient of the Cell Constant, namely,

$$\frac{1}{K} \frac{dK}{dt} = (\beta - 2\gamma) + \frac{s}{l} (\beta - \gamma) \quad (66)$$

from which it is evident that the shorter the electrode stems the smaller will be the temperature coefficient of the cell.

*Cells of Type C.*—If the diameter of the cross-section of the connecting tube is small in comparison with its length, we have approximately

$$\frac{dl}{dt} = l\beta \quad (67)$$

and

$$\frac{dA}{dt} = 2A\beta \quad (68)$$

and hence from Equation 63

$$\frac{1}{K} \frac{dK}{dt} = -\beta \quad (69)$$

*Cells of the Arrhenius Type.*—For this type we have

$$\frac{dl}{dt} = l\beta \quad (70)$$

and

$$\frac{dA}{dt} = 2\gamma A \quad (71)$$

and on combining with Equation 63 we have

$$\frac{1}{K} \frac{dK}{dt} = \beta - 2\gamma \quad (72)$$

*Typical Illustrations.*—The value of  $\gamma$  between  $0^\circ$  and  $100^\circ$  is  $9 \cdot 10^{-8}$ . For  $s$  we may safely put 2 cm. as the maximum value which the requirements of manufacture or of filling and cleaning will ever demand. Using these values Equation 66 may be written

$$\frac{1}{K} \frac{dK}{dt} = (\beta - 18 \cdot 10^{-6}) + \frac{2}{l} (\beta - 9 \cdot 10^{-6}). \quad (73)$$

For materials such as fused quartz where  $\beta < 0.5 \cdot 10^{-6}$ , this reduces to

$$\frac{1}{K} \frac{dK}{dt} = -18 \cdot 10^{-6} (1 + \frac{1}{l}). \quad (74)$$

For Jena Apparatus Glass for which<sup>10</sup>  $\beta = 6 \cdot 10^{-6}$ , it becomes

$$\frac{1}{K} \frac{dK}{dt} = -6 \cdot 10^{-6} (2 + \frac{1}{l}). \quad (75)$$

In Table I are given the values of  $\frac{100}{K} \frac{dK}{dt}$ , the percentage increase in the Cell Constant per degree rise in temperature, for some typical cells constructed of quartz and of Jena Apparatus Glass, respectively. It will be noticed that these coefficients are very small and that they are all negative. By making  $s$  smaller than 2 cm., they could be decreased still further.

It seems reasonable to suppose that the coefficients calculated in this way will usually justify the use of two significant figures in expressing them; that is, the influence of the "edge effect" will in most cases not introduce an error as large as 10% in the calculated coefficient. If this statement is true, then it will be apparent that if the cell constant is known for one temperature, its value at another temperature may be safely calculated by means of the above relationships, from the equation

$$K_2 = K_1 (1 + (t_2 - t_1) \frac{1}{K} \frac{dK}{dt}) \quad (76)$$

provided that  $p_{K_1}$ , the permissible percentage error in  $K_1$ , fulfills the relation

$$p_{K_1} \geq \frac{10(t_2 - t_1) \frac{1}{K} \frac{dK}{dt}}{1 + (t_2 - t_1) \frac{1}{K} \frac{dK}{dt}} \quad (77)$$

it being, of course, also true that  $p_{K_1}$  cannot be less than  $p_{K_1}$ .

A check on the above considerations by means of an experimental study of the variation of Cell Constants with the temperature has not been made.

<sup>10</sup> A value kindly given me by Dr. E. C. Sullivan of the Corning Glass Works.

TABLE I.

Values of  $\frac{100}{K} \frac{dK}{dt}$ , the percentage increase in the cell constant per degree rise in temperature, for different types of cells in which the length of each electrode stem is taken to be 1 cm.

Type of cell. (See Sec. 8.)	$l$ in cms.	100/K $dK/dt$ .	
		Quartz $\beta = 0.44 \cdot 10^{-4}$ .	Jena App. Glass $\beta = 6 \cdot 10^{-4}$ .
A	0.2	—0.0103	—0.0042
A	0.3	0.0067	0.0032
B	1.8	0.0027	0.0015
B	< 10	0.0018	0.0012
C	*	0.000044	0.0006
Arrhenius	All values	0.0018	0.0012

\* For all cases where  $l$  is large in comparison with  $D$ , the diameter of the cross-section.

### 13. The Choice of the Material for Constructing a Conductivity Cell.—

The material of which the cell is composed must first of all be practically insoluble in the liquids to be used in the cell. For most aqueous solutions,<sup>11</sup> at temperatures not greater than 100° and at atmospheric pressure, fused quartz and a number of varieties of glass fulfill this condition satisfactorily. Fused quartz and Jena Apparatus Glass are the materials which have been most extensively used in this laboratory for conductivity work and a brief comparison of their relative merits is perhaps worth while.

The quartz is, of course, more resistant to the attack of water than is the glass, but Kohlrausch's investigation of the solubility of Jena Glass<sup>12</sup> demonstrated that it is sufficiently resistant for all purposes where the solutions are to be made up and handled in contact with the atmosphere. This is confirmed by our own experience with it.<sup>4</sup> Conductivity water with a specific conductance of  $0.21 \cdot 10^{-6}$  ohm has been kept in Jena Apparatus Glass for 12 hours without any appreciable change in its conductance and after several weeks' standing the conductance did not rise above  $0.6 \cdot 10^{-6}$  and in this case the contamination undoubtedly came from the atmosphere.

From the standpoint of cost of material and ease of construction the glass is, of course, to be preferred. A tight seal between the glass and the platinum is comparatively easy to make and is not likely to fracture if handled with ordinary care, and good cells can be made by any skilled glass blower. The manufacture of quartz cells, on the other hand, re-

<sup>11</sup> Such cases as solutions of hydrofluoric acid, solutions at very high temperatures and pressures and solutions of strong alkalies and acids, especially when hot, represent special cases which require individual treatment and they are, therefore, not included here.

<sup>12</sup> Kohlrausch, *Ber.*, 26, 2915, 2998 (1893).

quires the services of a skilled quartz worker and the operation of sealing in the platinum electrodes is covered by patents.

From the standpoint of the magnitude of the effect of temperature on the cell constant, quartz is superior to Jena Apparatus Glass for constructing cells of Type C. As shown in Table I, the cell constant of a quartz cell of this type changes only 0.004% for a 100° change in temperature. From the same point of view the glass is superior to the quartz in the case of cells of Types A and B, as shown by the data in the Table. By choosing a glass with the proper coefficient of expansion it is theoretically possible to construct cells of these types in which the cell constant will be practically independent of the temperature. The necessary condition is obtained by equating the right hand member of Equation 66 to zero, giving

$$\beta = \frac{2 + \frac{s}{l}}{1 + \frac{s}{l}} \gamma \quad (78)$$

or putting  $s = 2$  and  $\gamma = 9 \cdot 10^{-6}$

$$\beta = \frac{2 + \frac{2}{l}}{1 + \frac{2}{l}} \gamma. \quad (79)$$

According to the value of  $l$ ,  $\beta$  varies between  $18 \cdot 10^{-6}$  and  $9 \cdot 10^{-6}$ . Glass can be manufactured<sup>13</sup> with almost any coefficient of expansion between  $3 \cdot 10^{-6}$  and  $14 \cdot 10^{-6}$ , so that the above conditions could be met if desired.

Aside, however, from the desirability of having a cell constant with a small temperature coefficient, it is essential that the cell constant shall not exhibit appreciable thermal hysteresis. With respect to this quality, quartz would be superior to any glass and for this reason quartz is to be greatly preferred for all very accurate work at temperatures greatly removed from room temperature. For the same reason glass cells should be very carefully annealed and aged for a period before being put into use.

**14. The Elimination of Polarization.** (a) *By Platinization and Increase of Frequency.*—The elimination of the effects of polarization in conductivity measurements is usually effected by control of the frequency of the current and of the size and the extent and degree of platinization of the electrode surfaces. In all cases where the presence of platinum black is permissible it has been our experience that polarization can always be eliminated, even when using comparatively low frequencies ( $f > 1000$ ) by the usual process of platinizing the electrodes. It sometimes happens, however, that the solution under investigation contains a substance which

<sup>13</sup> Sullivan, *J. Soc. Chem. Ind.*, 35, 513 (1916).



undergoes a slow decomposition or oxidation in contact with platinum black. Under these circumstances, provided the solution is not too concentrated, the effect of polarization may frequently be eliminated by simply increasing the frequency until a sharp minimum is secured.

The effect of uncompensated polarization always manifests itself by the appearance of a poor minimum, silence never being obtained and a different quality of tone usually being apparent on the two sides of the minimum. In eliminating polarization by the customary device of platinizing the electrodes it should be remembered that the heavier the coating of platinum black the more difficult and tedious will the operation of washing the cell be. The platinum black coating should only be of sufficient thickness to accomplish the elimination of polarization in the solutions for which the cell is to be employed. At present this can only be determined by trial since the problem of the degree of platinizing as a function of the frequency of the current and the nature of the solution, its concentration and temperature is one which still awaits systematic investigation.<sup>14</sup>

In eliminating polarization by increase of frequency, the frequency employed should not be greater than necessary to accomplish the desired result owing to disturbances arising from capacity and inductive influences, which disturbances increase with increasing frequency. For frequencies between 1000 and 5000 cycles the sensitivity of the human ear is approximately constant.

For use in investigations in which it is necessary to eliminate polarization by increase of frequency, it is convenient to have available, telephones tuned to one or two of the higher frequencies, say 1800 and 3000 cycles. It is, of course, also necessary to employ a cell designed to fit the telephone at the particular frequency which is to be employed.

As an illustration of the effect of increasing the frequency, some results obtained in connection with a recently completed investigation in this laboratory, may be mentioned. It was necessary to measure the conductance of a 0.002 *N* salt solution containing organic substances which decomposed in contact with platinum black. Using a cell of Type B provided with sand blasted electrodes, the minimum obtained with 1000 cycles was not satisfactory but by increasing the frequency to about 1800 cycles it became perfectly sharp.

In eliminating polarization by increase of frequency it should, of course, be remembered that the presence of polarization is not the only factor which causes a poor minimum and before attributing a poor minimum to this cause, one should make sure that the resistances and the condensive and inductive reactances are properly balanced and symmetrically dis-

<sup>14</sup> A few experiments along this line using a solution of platinum chloride as the electrolyte have been made by Wien (*Ann. Phys.*, 58, 57 (1896)).

tributed in the bridge net work, and that the electromagnetic shielding has been properly carried out. A quick way of deciding whether a poor minimum is due to the incomplete elimination of polarization or not is to substitute in place of the cell in question a second cell<sup>15</sup> having heavily platinized electrodes and filled with a solution which will give it about the same resistance as the original cell. If the minimum does not become perfectly sharp it indicates that causes other than polarization are responsible. A discussion of some of these other causes and their elimination will be taken up in the third paper of this series which will deal with the details of bridge construction and assembly.

In this connection it should also be remembered that not only will the minimum be poor when polarization is present, but the center of that minimum, even if it can be accurately determined, does not represent the correct bridge setting, but differs from it by an amount  $\Delta R'_B$  which in our nomenclature is expressed by the equation<sup>16</sup>

$$\Delta R'_B = \frac{1/2 R_B}{(2\pi f C_p R)^2} \quad (80)$$

where  $C_p$  is the capacity equivalent of the polarization. As  $f$  increases  $C_p$  also increases and hence  $\Delta R'$  rapidly decreases. The elimination of polarization is thus not merely for the purpose of bettering the minimum but also for the purpose of obtaining a correct bridge reading.

(b) *By Compensation and Increase of Frequency.*—For the measurement of the specific resistance of a good conductor in which for any reason the presence of platinum black is not allowable, the method of merely increasing the frequency ceases to be practicable owing to the lack of sensitivity of the telephone for the very high frequencies which would be required. In such a case, however, a method originally suggested by Kohlrausch and later developed and used by Wien is available. This method is based upon the electrical compensation of the polarization.

In so far as polarization acts like a pure condensive reactance in series with the cell it should be possible theoretically to eliminate it either by the insertion of a variable pure inductance in series with the cell, as was early suggested by Kohlrausch; or by the insertion of a variable capacity in series with the resistance box, as in the dielectric-constant method of Nernst.<sup>17</sup> Since the second method is impracticable for good conductors, owing to the magnitude of the capacity required, Wien took up the experimental study<sup>18</sup> of the first method, and he soon discovered that the

<sup>15</sup> A cell with heavily platinized readily adjustable electrodes would be convenient for this test.

<sup>16</sup> For the deduction and discussion of this equation and a number of experiments illustrating the magnitude of  $\Delta R'$  for different frequencies see Wien, *Wied. Ann.*, **47**, 627 (1892).

<sup>17</sup> Nernst, *Z. physik. Chem.*, **14**, 622 (1894).

<sup>18</sup> Wien, *Loc. cit.*, 1896, p. 37. See also Neumann, *Ibid* **67**, 499 (1899).

effect of polarization is not solely that of a pure condensive reactance but that an increase in effective resistance accompanies it. In other words the compensation of the condensive reactance arising from the polarization, while it improved the minimum, did not give the correct bridge setting but gave a value which corresponded to an apparent increase in the resistance of the cell. This apparent increase in resistance he found to be the smaller, the larger the electrodes and the higher the frequency, and he suggested the very plausible hypothesis that it arises from the incomplete reversal of the electrode reaction. Such a failure of the electrode reaction to reverse itself would mean the consumption of energy and in an alternating current circuit this would play the same role as ohmic resistance. Moreover, it would become less and less as the frequency increased.<sup>19</sup>

By Wien's device, therefore, of electrically compensating for the condensive reactance of the polarization and increasing the frequency so as to eliminate as far as possible the energy loss, arising probably from the incomplete reversal of the electrode reactions, he was able to secure very satisfactory measurements of good conducting solutions with un-platinized electrodes. These results of Wien have been recently reproduced with modern apparatus at the Bureau of Standards by Curtis and Taylor<sup>20</sup> who found that the above method applied to 0.1 *N* and 0.05 *N* solutions of NaCl gave, within 0.02%, the same ratio of specific conductances as was obtained with platinized electrodes.<sup>21</sup>

In concluding this discussion of the conductivity cell, it seems worth while to call attention to the need of a new determination of the absolute specific conductance of some solution. For the purpose of obtaining cell constants we are at present dependent upon Kohlrausch's determination of the specific conductance of potassium chloride solutions. It is doubtful if his values are as accurate as 0.05%. With modern apparatus the accuracy with which these values can be determined is limited only by the accuracy with which the salt could be purified and the solutions made up. It is to be hoped that some institution, such as our National Bureau of Standards for example, will before long undertake the repetition of Kohlrausch's measurements of the specific conductance of the material best suited for use as a standard in determining cell constants.

In conclusion I wish to acknowledge the assistance of Mr. H. J. Weiland and Mr. J. M. Braham in checking the algebra and arithmetic involved in the calculations given in this paper. Most of these calculations have

<sup>19</sup> In this connection the thought naturally occurs that the efficiency of platinum black in eliminating polarization in conductivity measurements is not due solely to the increase in the area of the electrode but arises in part from its catalytic powers.

<sup>20</sup> Curtis and Taylor, *Phys. Rev.*, 6, 64 (1915).

<sup>21</sup> A third method for diminishing the influence of polarization has been described by Wolcott, *Ann. Phys.*, 12, 1653 (1903).

been checked by both men and it is believed that the values given are correct.

URBANA, ILLINOIS.

## REVIEW: THE PREPARATION OF CONDUCTIVITY WATER.<sup>1</sup>

By JAMES KENDALL.

Received June 30, 1916.

Water so nearly corresponds to the universal solvent sought by the alchemists that it is a matter of extreme difficulty, whatever methods of purification are adopted, to obtain a sample which may be shown to be practically free from all conducting impurities. Still more onerous is the task of preserving such a specimen when once prepared, since solution from the containing vessel inevitably introduces some contamination. The final and practical object—to maintain the sample at its original purity while actually in use in conductivity determinations—borders closely upon the unattainable.

By repeated distillations *in vacuo* Kohlrausch and Heydweiller,<sup>2</sup> working in Strasbourg,<sup>3</sup> succeeded in obtaining, in a glass conductivity cell, water with a specific conductivity of  $0.043 \times 10^{-6}$  reciprocal ohms at 18°, or  $0.015 \times 10^{-6}$  reciprocal ohms at 0°.<sup>4</sup> These values are certainly very near to those which would be given by perfectly pure water at the corresponding temperatures. This has been proved by the employment of several distinct indirect methods for determining the ionization constant of water.<sup>5</sup> Kohlrausch and Heydweiller themselves estimate the specific conductivity of absolutely pure water at 18° to be  $0.0384 \times 10^{-6}$  reciprocal ohms.<sup>6</sup>

If it were possible to reproduce this work conveniently and, after obtaining in quantity water of such extreme purity, to employ it in actual conductivity work, then it is obvious that we should never need to apply to our results any water correction at all.<sup>7</sup> In order to do this, however,

<sup>1</sup> Nearly all chemists have occasion at some time to employ especially pure water in their investigations, and find that the usual methods often fail to give the anticipated results. It is difficult to collect from the references in the literature (since the work is generally only incidental) satisfactory suggestions in such a case. Perhaps the most frequent mistake made is to persist in the attempt to prepare water beyond the laboratory's limit of purity. In the following pages the previous work on the subject is summarized and the utmost degree of purity attainable under ordinary conditions indicated.

<sup>2</sup> Kohlrausch and Heydweiller, *Z. physik. Chem.*, **14**, 326 (1894).

<sup>3</sup> After each reference which follows, the place where the investigation was carried out will be indicated. The difficulty in obtaining good conductivity water varies considerably in different localities, as will be seen below.

<sup>4</sup> One millimeter of this water at 0° possessed a resistance equal to that of forty million kilometers of copper wire of the same sectional area, or a length of wire capable of encircling the earth a thousand times.

<sup>5</sup> Landolt-Börnstein, *Tabellen*, **1912**, p. 1187.

<sup>6</sup> This is often incorrectly quoted as the *experimental value* of Kohlrausch and Heydweiller. The results are also usually given without conversion from the Siemens units in which they were published to the units now employed.

<sup>7</sup> A general discussion of the water correction in conductivity determinations will

it would be essential to carry out all the manipulations (preparation of solutions and measurement of conductivities) in evacuated vessels. This is a feat which has been frequently attempted but, owing to the extraordinary experimental difficulties involved, not yet successfully concluded.

The necessity for carrying out the whole of the work *in vacuo* arises from the fact that water, on exposure to the atmosphere, immediately loses its purity. Thus Kohlrausch and Heydweiller<sup>1</sup> give the following values from their experiments with two separate specimens:

Original spec. cond. of water *in vacuo* . . . . .  $0.05 \times 10^{-8}$  to  $0.11 \times 10^{-8}$

Spec. cond. after 20 min. exposure to air . . . . .  $0.34 \times 10^{-8}$  to  $0.40 \times 10^{-8}$

Spec. cond. after long exposure to air . . . . .  $0.66 \times 10^{-8}$  to  $0.65 \times 10^{-8}$

The final values obtained for different samples in equilibrium with the atmosphere were practically constant at  $0.65$  to  $0.70 \times 10^{-6}$  reciprocal ohms at  $18^\circ$ . Subsequent investigators have recorded uniformly similar results; it is impossible to maintain, for more than a short interval of time, any sample of water in contact with air at a much lower value. All existent conductivity data have consequently been obtained with the use of water of this order of purity.

While, therefore, Kohlrausch and Heydweiller accomplished the preparation of small quantities of exceedingly pure water, the main problem—the preparation of pure water in large quantity for actual conductivity determinations—was left unsolved. In later experimental work, indeed, Kohlrausch and Maltby,<sup>2</sup> recognizing the futility of preparing extremely pure water which would be sure to become contaminated before use, did not attempt any further refinements of method, but employed water which was obtained in bulk from Kahlbaum in Berlin with a specific conductivity of  $0.8$  to  $1.0 \times 10^{-6}$  reciprocal ohms at  $18^\circ$ . The water correction for such a sample at high dilutions is considerable.<sup>3</sup>

The endeavors of subsequent investigators have been almost entirely directed towards the facile preparation of large quantities of water of as low a specific conductivity as is possible *in contact with air*. The uncertain water correction consequent upon the employment of such water for conductivity work at high dilutions has come to be regarded as an unavoidable evil. The main investigations of this nature, the methods followed and the results obtained are summarized below.

Walker and Cormack,<sup>4</sup> in Dundee, prepared water of specific conductivity  $0.75 \times 10^{-6}$  at  $18^\circ$  by three successive distillations—with alkali, with phosphoric acid, and without the addition of any chemical. No lower permanent value, it was shown, could be obtained for water in contact with air.

Kohlrausch,<sup>5</sup> in Berlin, found that the specific conductivity of water at  $18^\circ$  was lowered from  $0.9 \times 10^{-6}$  to  $0.5 \times 10^{-6}$  by long standing in an appear in a subsequent communication, to which this and a former article (Kendall, *THIS JOURNAL*, 38, 1480 (1916)) are preliminary.

<sup>1</sup> Kohlrausch and Heydweiller, *Ann. Physik*, 53, 209 (1894).

<sup>2</sup> Kohlrausch and Maltby, *Wiss. Abhandl. Physik-Techn. Reichsanstalt*, 3, 188 (1900).

<sup>3</sup> See Kraus and Bray, *THIS JOURNAL*, 35, 1413 (1913).

<sup>4</sup> Walker and Cormack, *J. Chem. Soc.*, 77, 5 (1900).

<sup>5</sup> Kohlrausch, *Z. physik. Chem.*, 42, 193 (1902).

atmosphere free from carbon dioxide. When  $\text{CO}_2$ -free air was passed through such water in the conductivity cell, the specific conductivity fell further to  $0.2\text{--}0.3 \times 10^{-6}$  but reverted soon to the higher value if the water was again exposed to the atmosphere.

Bousfield,<sup>1</sup> at Hendon (near London), prepared water of specific conductivity  $1.0 \times 10^{-6}$  at  $18^\circ$  by a process of continuous fractional distillation. The most favorable results were obtained by addition of a trace of  $\text{KHSO}_4$  to keep back ammonia and basic impurities. Later improvements<sup>2</sup> gave water of specific conductivity  $0.8 \times 10^{-6}$  in one distillation from tap-water without the use of any chemicals.

Hartley, Campbell and Poole<sup>3</sup> have described an apparatus which supplies water of specific conductivity  $0.75 \times 10^{-6}$  (at  $18^\circ$ ) in a single distillation from Oxford tap-water. Bourdillon,<sup>4</sup> also working at Oxford, has improved greatly upon this and has obtained water of specific conductivity less than  $0.2 \times 10^{-6}$  (part of the yield being as low as  $0.09 \times 10^{-6}$ ) by a single distillation into an air-tight cell. So long as the water was kept in this cell, its specific conductivity increased only slowly (for example, from  $0.12 \times 10^{-6}$  to  $0.4\text{--}0.45 \times 10^{-6}$  in 2–3 weeks), but if the cell was not air-tight the conductivity rose rapidly.

Paul,<sup>5</sup> in Munich, has also recently described a method of obtaining water of specific conductivity  $0.8 \times 10^{-6}$  at  $18^\circ$  by one distillation.

In this country the chief conductivity work at high dilutions has been carried out at the Massachusetts Institute of Technology by A. A. Noyes and his coworkers. Noyes and Coolidge<sup>6</sup> have described a very efficient still for the preparation of high-grade conductivity water. Washburn,<sup>7</sup> using this still at Urbana, has obtained water of specific conductivity  $0.4 \times 10^{-6}$  at  $0^\circ$  and  $0.6 \times 10^{-6}$  at  $25^\circ$  by distillation from an alkaline permanganate solution. The purest water employed by Goodwin and Haskell,<sup>8</sup> at Boston, in their work on hydrochloric and nitric acids at high dilutions, possessed a specific conductivity of  $0.8 \times 10^{-6}$  at  $18^\circ$ .

### Experimental.

The general results of previous workers indicate that, while it is a comparatively easy matter to obtain water of specific conductivity  $0.7\text{--}0.8 \times 10^{-6}$  at the ordinary temperature ( $18^\circ$ ), special apparatus and stringent precautions are necessary to effect any further purification. The significance of the constancy of the values obtained for water in contact with air by different observers working in different laboratories and using different methods has been discussed in a preceding paper.<sup>9</sup>

Sufficient attention does not seem to have been called to the fact that

<sup>1</sup> Bousfield, *J. Chem. Soc.*, **87**, 740 (1905).

<sup>2</sup> Bousfield, *Ibid.*, **101**, 1443 (1912).

<sup>3</sup> Hartley, Campbell and Poole, *Ibid.*, **93**, 428 (1908).

<sup>4</sup> Bourdillon, *J. Chem. Soc.*, **103**, 791 (1913).

<sup>5</sup> Paul, *Z. Elektrochemie*, **20**, 179 (1914).

<sup>6</sup> Noyes and Coolidge, *Proc. Am. Acad.*, **39**, 190 (1908).

<sup>7</sup> Washburn and MacInnes, *THIS JOURNAL*, **33**, 1688 (1911); Washburn and Williams, *Ibid.*, **35**, 751 (1913); The above are average results. The specific conductivity at  $25^\circ$  increased from an initial value of  $0.19 \times 10^{-6}$  to a final value of  $0.60 \times 10^{-6}$  on exposure to air.

<sup>8</sup> Goodwin and Haskell, *Phys. Rev.*, **19**, 271. (1904).

<sup>9</sup> Kendall, *THIS JOURNAL*, **38**, 1480 (1916).

a method for the preparation of conductivity water which answers extremely well in one laboratory may not work at all in another. The reason lies presumably in the difference in the nature of the impurities present in different water supplies.<sup>1</sup>

While engaged in conductivity determinations at Edinburgh, in 1911-12, the present author found that several of the standard methods (*e. g.*, distillation from alkaline permanganate or repeated distillation without chemicals) failed to give water below  $1.2 \times 10^{-6}$  at  $25^\circ$  in spite of all precautions taken. The Edinburgh water supply was at that time notoriously contaminated with objectionable impurities,<sup>2</sup> the atmospheric conditions in the city are also not of the best.<sup>3</sup> Professor Walker suggested the addition of Nessler's solution to the water under distillation as a method for the simultaneous elimination of the two volatile conducting impurities most to be apprehended—ammonia and carbon dioxide. It was found that one distillation from tap-water to which a few cc. of Nessler's solution had been added provided water of specific conductivity  $0.9 \times 10^{-6}$  at  $25^\circ$ .

This distillation was carried out in the open air with Jena glass vessels and a block-tin condenser, specially modified to ensure thorough washing of the steam on the way to the receiver. By redistillation in silica vessels (connected with a ground-on silica hood),<sup>4</sup> no chemicals being added and the distillate being collected hot, water of specific conductivity  $0.2-0.6 \times 10^{-6}$  at  $25^\circ$  was obtained. Such low values could be observed, however, only when the distillate was tested at once, for its specific conductivity increased rapidly on standing until values of  $0.8-0.9 \times 10^{-6}$  at  $25^\circ$  were attained. The following series of measurements upon a sample of water transferred to a conductivity cell immediately after collection will illustrate this.<sup>5</sup>

Time after transference to cell.....	0.5 min.	2 min.	10 min.	1 hr.	2 hrs.	6 hrs.
Specific conductivity $\times 10^{-6}$ .....	0.22	0.30	0.39	0.55	0.69	0.80

On longer standing no appreciable change occurred; even after the water had remained in the cell for three weeks the specific conductivity was only  $0.85 \times 10^{-6}$ .

The same method of purification was subsequently employed successfully in other laboratories—in Stockholm, Petrograd and New York City.<sup>6</sup> It may therefore be recommended as an easy and general method for the preparation of high-grade conductivity water.

<sup>1</sup> Ostwald found that his measurements upon dilute solutions of acids, made in Riga, were in error owing to the presence of ammonia in the conductivity water employed. In Leipzig this difficulty vanished (*Z. physik. Chem.*, **2**, 280 (1888)).

<sup>2</sup> The purely scientific results obtained from a consequent examination of the water supply are to be found in a paper by Walker and Kay, *J. Soc. Chem. Ind.*, **31**, 1013 (1912).

<sup>3</sup> As its familiar name, "Auld Reekie," testifies.

<sup>4</sup> A still of this type can now be obtained from the Thermal Syndicate, Ltd., New York City.

<sup>5</sup> Specific conductivities have been reduced to  $25^\circ$  throughout to give comparable results.

<sup>6</sup> Results are tabulated in the preceding paper (Table XI). It may be noted that at Petrograd, also, other methods of water purification failed.

The results obtained throughout have been in entire agreement with those of previous investigators in confirming the conclusions of Kohlrausch. Water in contact with air possesses a specific conductivity of at least  $0.7-0.8 \times 10^{-6}$  at  $18^\circ$ , and the correction for this in conductivity determinations at high dilutions must be considerable. The elimination of the water correction by the preparation of perfectly pure water is therefore doomed to remain impracticable unless the whole work is carried out in air-tight vessels. In this connection, present investigations by Washburn at Urbana and by Hartley at Oxford may be mentioned. Hartley and Bassett<sup>1</sup> have already described an "intermediate" type of apparatus for use with very dilute solutions—successive small quantities of solute being added to a large volume (300 cc.) of solvent contained in a special cell which protects it from contamination with the air. The cells designed by Washburn<sup>2</sup> are simpler and serve the same purpose.

#### The Carbonic Acid Concentration of "Pure Water."

In the preceding article<sup>3</sup> it has been shown that the purest distilled water of the laboratory is, in point of fact, a saturated solution of carbonic acid under the partial pressure of the carbon dioxide in the atmosphere, and contains no other conducting impurities in appreciable amount. Some additional evidence from the work of other observers as to the validity of the above conclusion may be considered here.

Caldwell,<sup>4</sup> in an examination of the Letts and Blake method for the determination of  $\text{CO}_2$  in air, made the following observations: "To ordinary distilled water more than sufficient KOH was added to make it alkaline. It was then distilled, and portions of the distillate examined from time to time. They were at first alkaline, no doubt from ammonia, but then became acid, and eventually of a *constant* degree of acidity. This degree of acidity was found to correspond with the amount of carbonic anhydride in the laboratory in which the water was distilled." Solubility measurements follow which confirm these statements.<sup>5</sup>

A recent paper by Fales and Nelson<sup>6</sup> also affords interesting results. According to theory, the hydrogen-ion concentration of *pure* water at  $25^\circ$  is a little less than  $10^{-7}$  normal. The purest distilled water of the laboratory<sup>7</sup> gave a hydrogen-ion concentration of  $10^{-6.8}$ . A saturated solution of carbonic acid under atmospheric conditions at  $25^\circ$  possesses a calculated ionic concentration of  $2.05 \times 10^{-6}$  (see the table on p. 2465). The hydrogen-ion concentration of such a solution,  $10^{-5.7}$ , is clearly in very close agreement with the observed value.

<sup>1</sup> Hartley and Bassett, *J. Chem. Soc.*, **103**, 789 (1913).

<sup>2</sup> "The Measurement of Conductivity of Electrolytes," Leeds and Northrup Co., Catalogue 48.

<sup>3</sup> Kendall, *Loc. cit.*

<sup>4</sup> Letts and Blake, *Proc. Roy. Soc. Dublin*, **9**, 222-3 (1900).

<sup>5</sup> The calculations as carried out by Caldwell are not accurate, since it is assumed that Henry's law in its simple form can be applied (see Kendall, *Loc. cit.*, page 1493). The true calculated values are in slightly better agreement with the observed.

<sup>6</sup> Fales and Nelson, *THIS JOURNAL*, **37**, 2782 (1915).

<sup>7</sup> The author's method of distillation from Nessler's solution was employed. It may be noted that the hydrogen-ion concentration of the indicator used (*p*-nitrophenol) would, under the conditions of experiment, be almost entirely suppressed in the presence of the stronger carbonic acid.



The results of the previous communication may be summarized in the following table:

SYSTEM: CO <sub>2</sub> -H <sub>2</sub> O (ATMOSPHERIC CONDITIONS).				
Temp.	Conc. of satd. soln. (mols per liter).	Ionization constant of H <sub>2</sub> CO <sub>3</sub> .	Conc. of ionized solute.	Spec. cond. of satd. solution.
0°.....	$2.94 \times 10^{-6}$	$2.24 \times 10^{-7}$	$2.46 \times 10^{-6}$	$0.65 \times 10^{-6}$
18°.....	$1.67 \times 10^{-6}$	$3.12 \times 10^{-7}$	$2.13 \times 10^{-6}$	$0.75 \times 10^{-6}$
25°.....	$1.40 \times 10^{-6}$	$3.50 \times 10^{-7}$	$2.05 \times 10^{-6}$	$0.80 \times 10^{-6}$

The agreement of the values given in the last column with those directly obtained by conductivity measurements is evident from Table XI of the preceding paper. Their agreement with the general results of other observers may be seen on examination of the values given in the review of previous work above. The fact that pure distilled water is a saturated solution of carbonic acid may therefore now be regarded as definitely established. If due precautions are taken, no other conducting impurity (such as ammonia from the original water supply or dissolved salts from the containing vessel), can be present in appreciable amount.<sup>1</sup>

It will be impossible to obtain *permanent* conductivity values for water in contact with air lower than those given in the above table. Many investigators have certainly employed "purer water" (*i. e.*, water of lower conductivity) in their measurements, but it is questionable whether any increase in accuracy has been gained thereby. Such water (prepared by passing CO<sub>2</sub>-free air through good distilled water) will be *unsaturated* with respect to the carbon dioxide content of the atmosphere, and will therefore slowly absorb CO<sub>2</sub> and consequently change in conductivity during the necessary manipulations. It is preferable to use a stable sample of water for which we can make an *exact* correction,<sup>2</sup> than to strive after a purer but unstable sample for which the correction is smaller but unknown.

This conclusion may be emphasized by a quotation from Kohlrausch:<sup>3</sup> "The purer the water, the more the difficulties of keeping it constant accumulate. Vessels with quite tight stopcocks would be necessary, if the employment of a purer water than that existing in contact with air (specific conductivity =  $0.8 \times 10^{-6}$  [at 18°] in the most favorable circumstances) is not to entail more dangers than advantages."

### Summary.

The results of previous work upon the preparation of conductivity water have been collected and discussed. A method has been described for obtaining a standard product of specific conductivity  $0.9 \times 10^{-6}$  at 25° by one distillation from tap-water. This method has been found to afford satisfactory results in four different laboratories.

It has been shown that the above specific conductivity value is the same as that given by a saturated solution of carbonic acid under atmospheric conditions. A permanent lower value for water in contact with air is not possible, since slow absorption of CO<sub>2</sub> must take place—unless airtight vessels are employed—until equilibrium is attained.

<sup>1</sup> If other impurities are present, then the observed conductivity will be in excess of that indicated above.

<sup>2</sup> As will be shown in a following paper.

<sup>3</sup> Kohlrausch, *Z. physik. Chem.*, 42, 200 (1902). See also Kohlrausch and Holborn, "Leitvermögen der Elektrolyte," pages 111-112 (Leipzig, 1898).

It is, indeed, quite unnecessary in conductivity work to invite the troubles involved in the preparation of purer water than the saturated  $\text{H}_2\text{CO}_3$  solution. The aim should rather be to exclude all other conducting impurities except  $\text{H}_2\text{CO}_3$ , and make for this an *exact* correction. The application of such a correction to electrolytes of different types at very high dilutions will be discussed in a succeeding article.

NICHOLS LABORATORIES OF INORGANIC CHEMISTRY,  
COLUMBIA UNIVERSITY, NEW YORK CITY.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

## THE HYDROLYSIS OF HEXAHYDROPYRIMIDINE.

BY GERALD E. K. BRANCH.

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### Introduction.

The study of the catalytic action of hydrogen ion has been recently extended to many cases in which the hydrogen ion decreases instead of increasing the speed of the reactions. The most notable of these investigations have been carried on by Biddle and his co-workers.

It appears that it is by no means uncommon for hydrogen ion to have a retarding effect. In fact in the case of additions to a nitrogen-carbon linkage, it might be expected from theoretical grounds that  $\text{H}^+$  should act as a negative catalyst when there is a tautomeric change involving the nitrogen atom. An example of such a reaction was found by Titherley and Branch<sup>1</sup> in the hydrolysis<sup>2</sup> of hexahydropyrimidine. It was there shown that this substance is tautomeric with methylene- $\alpha,\gamma$ -diaminopropane and that its hydrolysis to formaldehyde and trimethylenediamine is negatively catalyzed by hydrogen ion. Although they did not study this reaction quantitatively, they suggested that the effect of hydrogen ion was due to its favoring the less readily hydrolyzable ring form, a suggestion which has been verified by the author.

When an allelotropic mixture undergoes a reaction which is slow enough to allow equilibrium to be maintained between the isomers, any change in conditions which affects this equilibrium must have a corresponding influence on the reaction. In cases which involve a tautomeric shift about a nitrogen atom the isomers will show very different tendencies to form ions of the type of ammonium ion. The ability to add by virtue of a change of valence of the nitrogen varies inversely with the ability to add at the carbon nitrogen bond. Thus pyridine is a weaker base than piperidine but stronger than imines, just as benzene shows greater powers of addition than cyclohexane, but less than ethylenes.

<sup>1</sup> *J. Chem. Soc.*, 103, 330 (1913).

<sup>2</sup> In this paper hydrolysis is assumed to be preceded by an addition. For the argument, however, it is only necessary that it be a reaction which takes place more readily at a double than at a single bond.

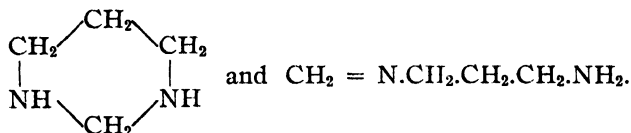
In an allelotropic mixture between the substances  $\text{HA}-\text{CH}=\text{NR}$  and  $\text{A}=\text{HC}-\text{NHR}$  and their hydrogen ion compounds  $\text{H}-\text{A}-\text{CH}=\text{N}^+\text{HR}$  and  $\text{A}=\text{HC}-\text{N}^+\text{H}_2\text{R}$ , where A and R represent any groups, the following equilibria are established:  $\text{HA}-\text{CH}=\text{NR} \rightleftharpoons \text{A}=\text{HC}-\text{NHR}$ ,  $\text{HA}-\text{CH}=\text{N}^+\text{HR} \rightleftharpoons \text{A}=\text{HC}-\text{N}^+\text{H}_2\text{R}$ ,  $\text{HA}-\text{CH}=\text{NR} + \text{H}^+ \rightleftharpoons \text{HA}-\text{CH}=\text{N}^+\text{HR}$ , and  $\text{A}=\text{HC}-\text{NHR} + \text{H}^+ \rightleftharpoons \text{A}=\text{HC}-\text{N}^+\text{H}_2\text{R}$ , and from the laws of equilibrium there will be the following relationships among the concentrations of the substances:

$$\frac{(\text{A}=\text{HC}-\text{NHR})}{(\text{HA}-\text{CH}=\text{NR})} = k_1, \quad \frac{(\text{A}=\text{HC}-\text{N}^+\text{H}_2\text{R})}{(\text{HA}-\text{CH}=\text{N}^+\text{HR})} = k_2,$$

$$\frac{(\text{HA}-\text{CH}=\text{N}^+\text{HR})}{(\text{HA}-\text{CH}=\text{NR})x(\text{H}^+)} = k_3 \quad \text{and} \quad \frac{(\text{A}=\text{HC}-\text{N}^+\text{H}_2\text{R})}{(\text{A}=\text{HC}-\text{NHR})x(\text{H}^+)} = k_4$$

Hence  $k_1 = \frac{k_3}{k_4} k_2$ , and since it has been shown above that  $k_4$  is greater than  $k_3$ , it follows that  $k_2$  is greater than  $k_1$ . Since an increase in concentration of hydrogen ion must favor the ionic forms, it decreases the proportion in which the double bond is situated between carbon and nitrogen, and consequently retards any additions taking place at the carbon-nitrogen linkage, insofar as its action is due to its effect on the equilibrium between the tautomers.

In the case of hexahydropyrimidine the tautomerism is between



Hydrogen ion, according to the rules given above, will greatly favor the former, while only the latter, in virtue of its double bond, will hydrolyze at an appreciable rate. This case is further complicated by the fact that methylene- $\alpha,\gamma$ -diaminopropane undergoes polymerization.<sup>1</sup> Acid solutions will contain chiefly hexahydropyrimidine as its disalt, but there will also be some monosalt of methylene- $\alpha,\gamma$ -diaminopropane and its polymers. It is only these latter substances which are directly acted on during hydrolysis, but as they are removed the hexahydropyrimidine reforms them until it also has disappeared. It will be shown later that the rates of the hydrolysis under different conditions of hydrogen ion concentration and temperature agree with this representation of its mechanism.

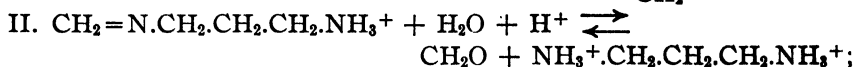
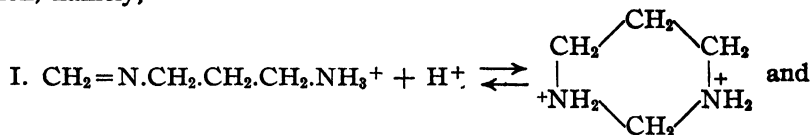
### The Nature of the Relation.

It has been shown by Titherley and Branch that when the hydrochloride of methylene- $\alpha,\gamma$ -diaminopropane is allowed to stand with an excess of mineral acid, and afterwards titrated with alkali, using methyl orange

<sup>1</sup> Titherley and Branch, *J. Chem. Soc.*, 103, 332 (1913).

as the indicator, a slow change takes place, which results in the neutralization of an equivalent of acid, and that the rate of the change is an inverse function of the acid concentration.

They suggested two reactions which might account for this phenomenon, namely,



and expressed the opinion that it was due to a combination of these two causes. They obtained evidence that both of these reactions could take place, and positive evidence that the phenomenon was at least in part due to the latter. However, they obtained no evidence that the former was not an almost immediate reaction, and hence could not account for the slow neutralization, and owing to its reversal its effect could not be observed by the above experiment.

That this reaction is, in fact, too fast to account for a slow change is shown by the following experiment. A solution of the hydrochloride of methylene- $\alpha,\gamma$ -diaminopropane was added to a solution containing methylviolet and enough hydrochloric acid to give a green color. The color immediately changed to a blue, corresponding to the neutralization of an amount of acid equivalent to the hydrochloride added, according to Equation I.

There was no noticeable further change of color after standing for more than an hour.

#### Experimental Method.

Solutions of trimethylene diamine, formaldehyde, and hydrochloric acid were mixed in equimolecular proportions. The resulting mixture is chiefly a solution of the hydrochloride of methylene- $\alpha,\gamma$ -diaminopropane, in equilibrium with small quantities of  $\text{CH}_2\text{O}$  and  $\text{NH}_2.\text{CH}_2.\text{CH}_2.\text{CH}_2.\text{NH}_2$ ,  $\text{HCl}$ , and also some other products of the union of the two latter substances.

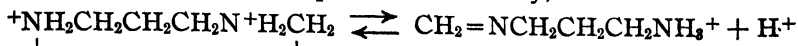
Measured volumes of this solution and standardized  $\text{HCl}$  were mixed and immersed in a thermostat. After an interval of from five to ten minutes<sup>1</sup> 20 cc. portions were withdrawn, from time to time, run into a mixture of ice and salt, and titrated, as rapidly as possible, with a 0.1 *N* solution of  $\text{NaOH}$ , using methyl orange as the indicator.

A peculiar phenomenon was observed during this titration. The solu-

<sup>1</sup> Rough estimates of the methylene- $\alpha,\gamma$ -diaminopropane in the original solution, made by calculating the amount hydrolyzed in this interval, give about 90% of a quantitative yield.

tion just becomes yellow, then changes back to pink; on further standing the solution again becomes yellow, even (although more slowly) when the solution is kept in a freezing mixture.

There are four possible explanations. Firstly, the reaction



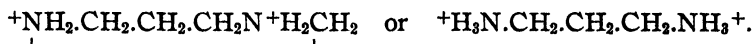
may be slow enough at this temperature,  $-5^\circ$  to  $-10^\circ$  to be noticeable. Secondly, the hydrolysis of  $\text{NH}_3^+\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_3^+$  may be slow. Thirdly,<sup>1</sup>  $\text{CH}_2\text{O}$  may form a compound with  $\text{H}^+$  which decomposes at a noticeable rate. Fourthly,  $\text{CH}_2\text{O}$  may have combined with  $\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$  in the original condensation to form traces of compounds more readily hydrolyzable than  $\text{CH}_2=\text{NCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ . If this were the case, during hydrolysis these substances would be reduced to concentrations which are no longer in equilibrium with the  $\text{CH}_2=\text{NCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$  in a neutral solution, and must reform, on neutralization, by the union of  $\text{CH}_2\text{O}$  with  $\text{NH}_3^+\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_3^+$  or  $\text{CH}_2=\text{NCH}_2\text{CH}_2\text{CH}_2\text{NH}_3^+$ , to give  $\text{H}^+$ . Further hydrolysis would then take place, reducing the  $\text{H}^+$  concentration, until a state of equilibrium is reached.

The first explanation is untenable, as the formation of acid becomes more marked as the hexahydropyrimidine is used up by hydrolysis. The second and third explanations can be shown to be unsound by the fact that neither solutions of  $\text{CH}_2\text{O}$  nor of  $\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ , when allowed to stand with excess of  $\text{HCl}$  and rapidly neutralized in the presence of ice and salt, become acid to methyl orange on standing. The last hypothesis is the only one which agrees with all the facts observed. In solutions in which all the hexahydropyrimidine has been hydrolyzed the acid formed after neutralization is permanent, also when solutions of  $\text{CH}_2\text{O}$  and  $\text{+H}_3\text{NCH}_2\text{CH}_2\text{CH}_2\text{NH}_3^+$  are mixed, there is a gradual formation of a small amount of  $\text{H}^+$ , which is permanent. In these cases the  $\text{H}^+$  is probably chiefly produced by the reaction  $\text{CH}_2\text{O} + \text{+H}_3\text{NCH}_2\text{CH}_2\text{CH}_2\text{NH}_3^+ \rightleftharpoons \text{CH}_2=\text{NCH}_2\text{CH}_2\text{CH}_2\text{NH}_3^+ + \text{H}^+$ .

For these reasons the first appearance of yellow was taken as the end point, and the titration was performed as rapidly as possible, and the solution vigorously agitated during the process. Naturally, accurate determinations cannot be made under these circumstances, but the measurements made after the reaction had been allowed to go to completion gave results within 5% of the theoretical amount of total amine.

The results at  $25^\circ$  are given in Table I. The first column gives the times from the first titration. The second column gives the concentration of acid as given by the titration. The last figure in this column gives the actual excess of acid above that necessary to form

<sup>1</sup> This explanation was suggested to the author by Dr. E. Q. Adams.



The third column gives the concentration of hexahydropyrimidine, and is obtained by subtracting the final from the actual acid titer. The significance of the fourth column will be discussed later. All concentrations are expressed in mols per liter.

TABLE I.—EXPERIMENTAL RESULTS AT  $25^\circ \pm 0.02^\circ$ .

Time in minutes.	Conc. of acid by titration.	Conc. of $CH_2=N.CH_2-CH_2.CH_2.NH_2$ . $K_2 \times 10^3$ .		Time in minutes.	Conc. of acid by titration.	Conc. of $CH_2=N.CH_2-CH_2.CH_2.NH_2$ . $K_2 \times 10^3$ .	
Experiment 1.				Experiment 5.			
0	0.1282	0.0291	..	0	0.3474	0.0482	..
4.92	0.1254	0.0263	3.32	24.83	0.3396	0.0404	4.40
13.75	0.1208	0.0217	3.59	78.75	0.3301	0.0309	3.64
28.75	0.1158	0.0167	3.46	$\infty$	0.2992	0	..
$\infty$	0.0991	0	..	Mean, 4.02			
Mean, 3.46				Experiment 6.			
0	0.0768	0.0140	..	0	0.2699	0.0769	..
12.67	0.07195	0.00915	3.66	12.25	0.2595	0.0665	3.27
32.58	0.06875	0.00595	3.43	26.83	0.2481	0.0551	3.57
$\infty$	0.0628	0	..	59.58	0.2316	0.0386	3.62
Mean, 3.55				$\infty$	0.1930	0	..
Experiment 3.				Mean, 3.49			
0	0.2031	0.0613	..	Experiment 7.			
6.33	0.1967	0.0549	3.32	0	0.1420	0.0402	..
18.17	0.1854	0.0436	3.82	6.92	0.1349	0.0331	3.92
31.67	0.1760	0.0342	3.98	26.00	0.1241	0.0223	3.69
$\infty$	0.1418	0	..	49.33	0.1165	0.0147	3.62
Mean, 3.71				$\infty$	0.1018	0	..
Experiment 4.				Mean, 3.74			
0	0.2505	0.0631	..	Experiment 8.			
8.33	0.2440	0.0566	3.89	0	0.1420	0.0402	..
20.42	0.2360	0.0486	3.87	6.92	0.1349	0.0331	3.92
54.33	0.2210	0.0336	3.78	26.00	0.1241	0.0223	3.69
$\infty$	0.1874	0	..	49.33	0.1165	0.0147	3.62
Mean, 3.85				$\infty$	0.1018	0	..

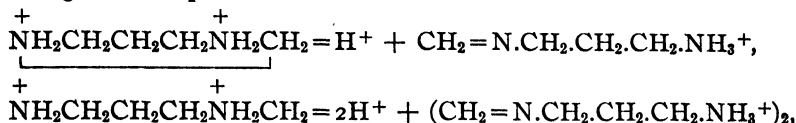
### Discussion of Results.

According to the mechanism suggested in this paper for the hydrolysis of hexahydropyrimidine, the rate of the reaction should depend on the concentrations of the various derivatives of its open chain tautomer, and should be given by the equation

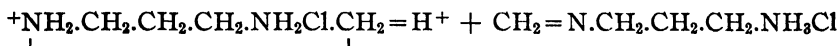
$$\frac{dx}{dt} = k_1 y_1 + k_2 y_2 + k_3 y_3 + \dots \quad (I)$$

where  $x$  represents the concentration of trimethylene diamine formed, and  $\gamma_1, \gamma_2$ , etc., represent the concentrations of the derivatives of methylene- $\alpha, \gamma$ -diaminopropane.

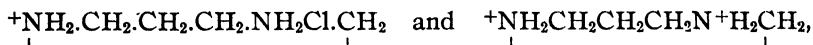
In dilute solutions, these substances will be present chiefly as their ions, which will be in equilibrium with the ion of hexahydropyrimidine according to the equations



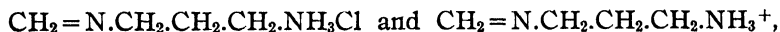
etc. Such an equilibrium as



may well be neglected, not only on account of the dilute nature of the solution, but also because owing to the similarity of



and of



such an equilibrium will be very similar to the corresponding equilibrium involving the fully ionized forms, and the rates of hydrolysis of



practically the same as that of



According to the laws of equilibrium, the concentrations of the various substances present will be related by the equations

$$\frac{\gamma_1(\text{H}^+)}{a} = k_{e1}, \quad \frac{\gamma_2(\text{H}^+)^2}{a^2} = k_{e2}, \quad \text{etc.}, \quad (2)$$

where  $\gamma_1$  is the concentration of  $\text{CH}_2 = \text{N}.\text{CH}_2.\text{CH}_2.\text{CH}_2.\text{NH}_3^+$ ,  $\gamma_2$  the concentration of  $(\text{CH}_2 = \text{N}.\text{CH}_2.\text{CH}_2.\text{CH}_2.\text{NH}_3^+)_2$ , and  $a$  the concentration of  $\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N}^+\text{H}_2\text{CH}_2$ .

Since in solutions whose concentrations of  $\text{H}^+$  are of the same order of magnitude as in those actually used there is but little diminution of  $\text{H}^+$  during the reaction, we have the following approximate relationships:  $a = (c_1 - x)\alpha_1$ , and  $(\text{H}^+) = c_2\alpha_2$ , where  $c_1$  is the initial concentration of hexahydropyrimidine in all its forms,  $\alpha_1$  the degree of ionization of its dihydrochloride,  $c_2$  the final concentration of  $\text{HCl}$ , and  $\alpha_2$  the degree of ionization of the  $\text{HCl}$ . Substituting in Equations 2 we get

$$\frac{\gamma_1 c_2 \alpha_2}{(c_1 - x)\alpha_1} = k_{e1}, \quad \frac{\gamma_2 (c_2 \alpha_2)^2}{\{(c_1 - x)\alpha_1\}^2} = k_{e2}, \quad \text{etc.}$$

For dilute solutions the approximate forms

$$\frac{y_1 c_2}{c_1 - x} = k_{e1}, \quad \frac{y_2 c_2^2}{(c_1 - x)^2} = k_{e2}, \text{ etc.}, \quad (3)$$

will introduce errors no greater than experimental. By combining Equations 1 and 3 we get the relationship

$$\frac{dx}{dt} = K_1 \frac{c - x}{c_2} + K_2 \frac{(c - x)^2}{c_2} + \dots \quad (4)$$

Neglecting all but the first two terms on the right-hand side of this equation (which corresponds to neglecting all polymers of methylene- $\alpha, \gamma$ -diaminopropane higher than dimolecular) and integrating gives

$$\frac{c_2}{K_1/K_2 t} \log \frac{c_1(c_1 - x + c_2 K_1/K_2)}{(c_1 - x)(c_1 + c_2 K_1/K_2)} = K_2.$$

The experimental results, substituted into this equation, give values for  $K_2$  constant within experimental error, for all values of  $K_1/K_2$  between  $1/2$  and  $1/4$ .  $K_2$  has therefore been calculated in this paper by assuming  $K_1/K_2 = 1/3$ .

The results at  $25^\circ$  have been collected in Table II, in which the first value obtained in each experiment has been neglected, except in the case of Experiment 2.

TABLE II.— $K_1/K_2 = 1/3$ . Temperature =  $25^\circ$ .

No. of Expt.	$c_1$	$c_1 - x$	$c_2$	$K_2 \times 10^3$
1.....	0.0291	0.0217	0.0991	3.59
1.....	0.0291	0.0167	0.0991	3.46
2.....	0.0140	0.00915	0.0628	3.66
2.....	0.0140	0.00595	0.0628	3.43
3.....	0.0613	0.0436	0.1418	3.82
3.....	0.0613	0.0342	0.1418	3.98
4.....	0.0631	0.0486	0.1874	3.87
4.....	0.0631	0.0336	0.1874	3.78
5.....	0.0482	0.0309	0.2992	3.64
6.....	0.0769	0.0551	0.1930	3.57
6.....	0.0769	0.0386	0.1930	3.62
7.....	0.0402	0.0223	0.1018	3.69
7.....	0.0402	0.0147	0.1018	3.62

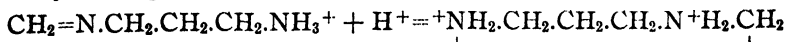
Mean, 3.67

### The Effect of Change of Temperature.

A study of the effect of the change of temperature on the rate of the reaction gives further corroboration of the mechanism suggested for the hydrolysis of hexahydropyrimidine. According to this theory, change of temperature should have an abnormally large effect on the rate, for not only will there be the usual increase of reaction rate with tempera-



ture, but there will be an increase in the concentrations of the substances actually undergoing hydrolysis, for the reactions



and



since they involve neutralization, are presumably exothermic. Also, since the heat of the latter reaction is probably the greater, it might be expected that the ratio  $K_1/K_2$  will decrease with rise of temperature. Unfortunately, this latter point cannot be decided from the data given in this paper, as the value  $K_1/K_2$  has not been obtained with sufficient accuracy. It has been shown, however, that the reaction has a high temperature coefficient. The mean value of  $K_2$  was found to be  $3.67 \times 10^{-3}$  at  $25^\circ$  and  $1.46 \times 10^{-3}$  at  $18.4^\circ$ , when  $K_1/K_2$  is assumed to be equal in both cases.

The results obtained at  $18.4^\circ$  are given in Tables III.

TABLE III.— $K_1/K_2 = 1/3$ . Temperature =  $18.4^\circ \pm 0.02^\circ$ .

Time in minutes.	Conc. of acid titration.	Conc. of $\text{CH}_2=\text{N}.\text{CH}_2.\text{CH}_2.\text{CH}_2.\text{NH}_2$ .	$K_2 \times 10^3$ .	Time in minutes.	Conc. of acid titration.	Conc. of $\text{CH}_2=\text{N}.\text{CH}_2.\text{CH}_2.\text{CH}_2.\text{NH}_2$ .	$K_2 \times 10^3$ .
Experiment 8.				Experiment 9 (continued).			
0	0.2065	0.0522	..	187.3	0.1455	0.0097	1.55
43.2	0.1948	0.0405	1.44	$\infty$	0.1358	0.0	..
90.0	0.1876	0.0333	1.28				
135.5	0.1812	0.0269	1.31				Mean, 1.49
$\infty$	0.1543	0.0	..				
		Mean, 1.34		Experiment 10.			
		Experiment 9.		0	0.2427	0.0494	..
0	0.1613	0.0255	..	163.5	0.2185	0.0252	1.54
60.75	0.1545	0.0187	1.42	231.0	0.2132	0.0199	1.53
117.8	0.1496	0.0138	1.50	$\infty$	0.1933	0.0	..
							Mean, 1.54

### The Effect of Alcohol and of Sodium Chloride.

Alcohol was found to accelerate the rate of this reaction. Dr. Lewis suggested to me that if alcohol, which is less electrophyllic than water, increased the rate, the addition of sodium chloride would probably have the reverse effect. This surmise proved to be correct when the concentrations of salt were high. However, low concentrations of salt increase the rate of hydrolysis. The results of one experiment in the presence of alcohol and four experiments in varying concentrations of sodium chloride are given in Table IV. In each case  $K_2$  has been calculated by the equation used in the previous experiments, and the same value for  $K_1/K_2$  assumed.

TABLE IV.— $K_1/K_2 = 1/3$ . Temperature =  $25^\circ$ .

Time in minutes.	Conc. of acids by titration.	Conc. of $\text{CH}_2=\text{N}.\text{CH}_2-\text{CH}_2.\text{CH}_2.\text{NH}_2$ .	$K_2 \times 10^4$ .	Time in minutes.	Conc. of acids by titration.	Conc. of $\text{CH}_2=\text{N}.\text{CH}_2-\text{CH}_2.\text{CH}_2.\text{NH}_2$ .	$K_2 \times 10^4$ .
Experiment 11. $\text{C}_2\text{H}_5.\text{OH} = 6.81 \text{ M.}$				Experiment 13. $\text{NaCl} = 0.1039 \text{ M.}$			
0	0.2215	0.0223	..	0	0.2222	0.0276	..
17.6	0.2113	0.0121	15.8	24.25	0.2145	0.0199	5.78
39.9	0.2065	0.0073	13.2	46.7	0.2100	0.0154	5.53
$\infty$	0.1992	0.0	..	$\infty$	0.1946	0.0	..
Mean, 14.5				Mean, 5.66			
Experiment 12. $\text{NaCl} = 0.0573 \text{ M.}$				Experiment 14. $\text{NaCl} = 0.173 \text{ M.}$			
0	0.2206	0.0279	..	0	0.2223	0.0278	..
10.9	0.2164	0.0237	6.17	22.9	0.2153	0.0208	5.39
32.4	0.2106	0.0179	5.87	45.75	0.2119	0.0174	4.49
71.8	0.2043	0.0116	5.50	$\infty$	0.1945	0.0	..
0.1927	0.0	..	..	Mean, 4.94			
Mean, 5.85				Experiment 15. $\text{NaCl} = 1.614 \text{ M.}$			
				0	0.2185	0.0322	..
				27.3	0.2136	0.0273	2.29
				53.6	0.2107	0.0244	1.99
				$\infty$	0.1863	0.0	..
				Mean, 2.14			

### Summary.

The effect of hydrogen ion on addition reactions of any allelotropic mixture, involving a tautomeric shift about a nitrogen atom, is discussed. It is pointed out that in such cases hydrogen ion may be expected to act as a negative catalyst.

The rate of hydrolysis of hexahydropyrimidine was measured under varying concentrations of hydrogen ion, and at two temperatures. Both the effect of hydrogen ion and of temperature on the rate of this reaction were found to be in agreement with this theory.

Alcohol was found to increase the rate of hydrolysis of hexahydropyrimidine.

Sodium chloride in low concentrations was found to increase the rate of this reaction, while in higher concentrations it acts as a negative catalyst.

BERKELEY, CAL.

### [CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA.] THE SILVER SALT OF TRIODOPHENOL AND ITS CATALYTIC DECOMPOSITIONS.

By G. H. WOOLLETT.

Received August 21, 1916.

In the course of further study of the catalytic decomposition of silver salts described by Hunter,<sup>1</sup> *et al.*, it became necessary to investigate the

<sup>1</sup> THIS JOURNAL, 38, 1761 (1916).

behavior of the silver salt of triiodophenol. On account of its symmetrical nature, it was expected that this salt would give a smooth catalytic decomposition, comparable to that of the salt of tribromophenol, giving

silver iodide, and a residue  $\text{---} \begin{array}{c} \text{H} \quad \text{I} \\ \diagdown \quad \diagup \\ \text{C} \quad \text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \text{I} \end{array} \text{---O---}$  which should then polym-

erize as did those already studied. Further, the result of this polymerization could not fail to be of interest, in comparison with the colored compound, of like empirical composition, already studied by several chemists, and now known as tetraiododiphenylenequinone.

This had been originally obtained by the action of iodine and sodium carbonate on phenol, by Lautemann<sup>1</sup> who believed it to be an aromatic oxide and called it diiodophenylene oxide. Kammerer and Benzinger<sup>2</sup> ascribed it to the formula of a tetraiododiphenoquinone,

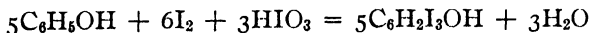
$\text{O} = \begin{array}{c} \text{I} \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C} \quad \text{C} \\ \diagup \quad \diagdown \\ \text{I} \quad \text{H} \end{array} = \begin{array}{c} \text{H} \quad \text{I} \\ \diagdown \quad \diagup \\ \text{C} \quad \text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \text{I} \end{array} = \text{O}$  and this formula has since been retained.

It is proposed to show in a later communication that this formula also is erroneous.

On making very pure samples of the silver salt, it was discovered that it was possible to obtain from it at will either a white amorphous product exactly like those described in the paper already cited, or a red substance, which was easily shown to be identical with Lautemann's red substance.

The present preliminary paper will contain a description of the properties of the silver salt, and of the conditions under which each of the above transformations occurs.

**The Silver Salt of Triiodophenol.**—The phenol was made by the following method, which is based on that of Körner:<sup>3</sup> One-fifth gram molecule of phenol and the amounts of iodine and iodic acid required by the equation



were each dissolved separately in a slight excess of 2 *N* potassium hydroxide solution. The three solutions were then mixed in a three-liter bottle with glass stopper, and diluted to two liters. To the solution dilute hydrochloric acid was slowly added, with good stirring. Iodine was liberated and at first very rapidly taken up, with formation of a white precipitate. After a while the color of free iodine remained for several minutes at a time. When this point was reached, the reaction mixture was rapidly made distinctly acid and placed on the shaking machine for two hours. The precipitate was then chiefly triiodophenol, colored with iodine, giv-

<sup>1</sup> *Ann.*, **120**, 309 (1861).

<sup>2</sup> *Ber.*, **11**, 557 (1878).

<sup>3</sup> *Ann.*, **137**, 214 (1878).

ing it a brown color. Dilute bisulfite solution was now added till the iodine color disappeared, and the precipitate was filtered off. It was a light pink, owing to the presence of a little of "Lautemann's red." This is formed by the action of free iodine on the alkaline solution.

The precipitate was dissolved in dilute alkali and filtered from the insoluble red substance. The mixture of triiodophenol with diiodophenol was reprecipitated from the filtrate by acetic acid, filtered, and washed. It was again dissolved in dilute alkali, treated with bone black without heating, and reprecipitated. It weighed about 80 g. It was purified by repeated solution in about 1500 cc. of alcohol and addition of an equal amount of water, until it gave the proper melting point, 156°. Less careful treatment yielded only products of much lower melting points. Our phenol agreed in every respect with the description of Körner.

From this very pure phenol a sample of silver salt was prepared in the usual way by precipitation from a solution of the potassium salt.

It was washed very carefully, dried on a porous plate, in the dark, then at 70° in a drying oven for nearly an hour, and finally over  $\text{CaCl}_2$  *in vacuo*. The sample was a full lemon yellow, with no appearance of change at any time during the procedure. It was analyzed for both silver and iodine by the method of Carius.

For Ag, subst., 0.1831 g.,  $\text{AgI}$  0.0737 g.; for I, subst., 0.1114 g.;  $\text{AgI}$ , 0.1355 g.

Calc. for  $\text{C}_6\text{H}_2\text{I}_3\text{OAg}$ : Ag, 18.65%; I, 65.82%. Found: Ag, 18.55; I, 65.72.

Since this salt is described by Hantzsch<sup>1</sup> as white in color, several attempts were made to obtain a colorless variety, without success. To see if the color might be due to an impurity, a sample of yellow salt was reduced by zinc and sulfuric acid, and the phenol so obtained was used to make another sample of silver salt, which was again yellow. On acidification of an ammoniacal solution, the yellow salt reappeared. Finally, silver nitrate was added to a glacial acetic acid solution of triiodophenol, when a yellow precipitate fell, which was collected, washed, and analyzed. It was low in silver, as was to be expected from its method of manufacture.

Subst., 0.1580 g.,  $\text{AgI}$ , 0.0587 g. Calc.: Ag, 18.65. Found: Ag, 17.08.

**Formation of the White Oxide from the Silver Salt.**—On treating the silver salt with cold ethyl iodide, most of it was converted into the normal ether triiodophenetole. However, the formation of a small amount of amorphous substance could be demonstrated. If the tendency of the silver salt to decompose was increased by heating, the desired catalytic decomposition occurred, as in the following experiment:

Three grams of good silver salt, in small lumps and powder, were heated about five minutes on the water bath, in an Erlenmeyer flask. Ten cc. of cold ethyl iodide were then poured on the salt. A vigorous reaction at

<sup>1</sup> *Ber.*, 40, 4875 (1905).

once resulted, in every respect analogous to those observed with the salt of tribromophenol and other phenols, except that the color was grass green instead of blue. The color lasted for about fifteen minutes. The silver iodide was filtered off, and on addition of ethyl alcohol to the filtrate, there resulted a slightly pink precipitate. A single solution in bromoform and reprecipitation removed the color, giving a white, amorphous powder, of properties similar to those of the polydibromophenylene oxide of Hunter, except for a less degree of solubility—for instance, it is almost insoluble in chloroform. It was carefully dried and analyzed.

Calc. for  $(C_6H_2I_2O)_n$ : I, 73.82%. Found: I, 73.60, 73.80. Carius subst., 0.1394, 0.1063; AgI, 0.1902, 0.1452.

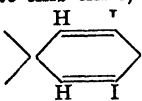
If both the salt and the ethyl iodide were heated before mixing, the action was very vigorous indeed, but gave the same white oxide. The pink color in the crude oxide was apparently due to the formation of a small amount of "Lautemann's red."

**"Lautemann's Red" from the Silver Salt.**—It was noticed that on long exposure to sunlight, the silver salt became red, suggesting the possibility of a second type of decomposition. Comparison with Lautemann's<sup>1</sup> method of making the red substance led to its preparation in the following manner:

A sample of the silver salt was ground up and suspended in water, and then treated with a single drop of a solution of iodine in potassium iodide. As the mixture was shaken, the silver salt became a dark purple in color, the solution still seeming to contain iodine. The colored solid residue was filtered off, dried, and extracted with carbon bisulfide. From this ligroin precipitated a dark red substance, entirely amorphous, and agreeing in every respect with samples made by the method of Lautemann. It was washed with alcohol, dried, and analyzed.

Subst., 0.1078; AgI, 0.1462. Calc. for  $(C_6H_2I_2O)_n$ : I, 73.82%. Found: 73.28.

That this formation of Lautemann's red instead of white amorphous substance is not due simply to the presence of iodine was easily shown by suspending dry salt in benzene, and adding a slight amount of iodine. This led to a formation of a white amorphous solid, only faintly tinged with pink, showing that iodine can also cause the formation of the white oxide. The question of the relation between the white and the red polymers of the unsaturated residues is being studied in this laboratory. It is perhaps worth pointing out, at this time, the possibility of a quinoid form

of the unsaturated residue,  = O although any effect that could be due to such a form, could also result by a simple shifting of val-

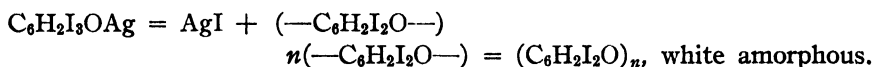
<sup>1</sup> *Loc. cit.*

ences without atomic rearrangement, after polymerization of the benzenoid form.

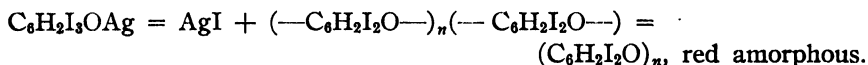
### Summary.

The silver salt of triiodophenol has been prepared in a very pure state, but the colorless form described by Hantzsch has not been obtained, all the samples found being yellow.

This salt, when warmed, gives with ethyl iodide a reaction exactly like that shown by the silver salt of tribromophenol, yielding silver iodide and an unsaturated residue which polymerizes to a white oxide.



The salt, when treated with a very little iodine in water, gives instead of the white oxide, the red substance first described by Lautemann.



MINNEAPOLIS, MINN.

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[CONTRIBUTION FROM THE LABORATORIES OF ORGANIC CHEMISTRY, UNIVERSITY OF ILLINOIS.]

## STUDIES OF TRIMETHYLENE OXIDE.

### I. PREPARATION AND CHARACTERIZATION.

By C. G. DERICK AND D. W. BISSELL.<sup>1</sup>

Received September 9, 1916.

I. Introduction. II. Preparation and Purification of Trimethylene Oxide. III. Properties of Trimethylene Oxide. IV. Proof of the Atomic Linking Structure. V. Experimental Part.

#### I. Introduction.

The use of ethylene oxide and its homologs in organic synthesis has been well established in the field of amino alcohols, and more recently their value in the Grignard reaction has been demonstrated by the work of Grignard,<sup>2</sup> Blaise,<sup>3</sup> and Henry.<sup>4</sup> In the study of the scale of influence of substitution, by the senior author and his students,<sup>5</sup> it is necessary to synthesize substituted monobasic paraffin acids, in which the substituents are further removed from the carboxyl group than the delta position. It seemed probable that trimethylene oxide would be of great value in effecting these syntheses. With this in mind the only reported synthesis of this substance was studied.

<sup>1</sup> Presented at the Urbana meeting of the American Chemical Society, 1916. From a thesis, submitted in partial fulfillment of the requirements for the degree of Master of Science at the University of Illinois.

<sup>2</sup> *Compt. rend.*, 136, 1260 (1903); 141, 44 (1905); *Ann. chim.*, [8] 10, 23 (1907).

<sup>3</sup> *Compt. rend.*, 134, 552 (1902).

<sup>4</sup> *Chem. Zentr.*, II, 445 (1907).

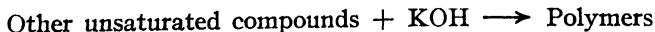
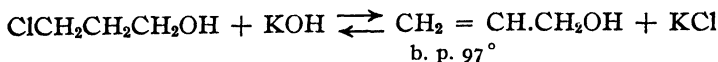
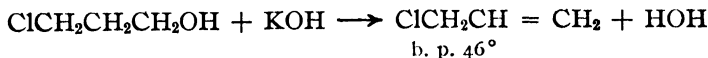
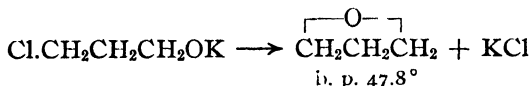
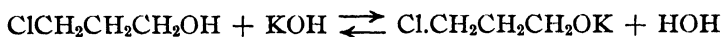
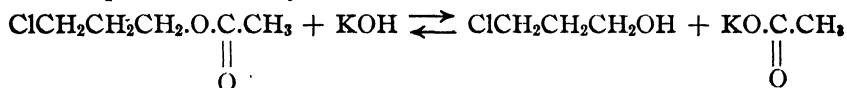
<sup>5</sup> THIS JOURNAL, 33, 1167 (1911); 38, 400 (1916).

The synthesis of trimethylene oxide by the action of a very concentrated solution of potassium hydroxide upon trimethylene chlorohydrin reported by Reboul<sup>1</sup> was repeated. The yield was very poor and the product very impure, as Section II will show. At best a yield of only 5% of the pure product could be obtained, even after many repetitions. These experiments suggest that Reboul never obtained the pure substance and accordingly the following study was undertaken.

## II. Preparation and Purification of Trimethylene Oxide.

Trimethylene oxide is best prepared by the action of potassium hydroxide containing 8% water upon gamma chloropropyl acetate at 100–110°. The desired products are condensed in a freezing mixture of hydrochloric acid and ice.

In order to purify the oxide it is necessary to know the different collisions of molecules that result in chemical reaction under the conditions of the experiment. They are as follows:



The physical properties of the substances resulting from the reactions show that this method of preparation gives trimethylene oxide contaminated with allyl alcohol, allyl chloride and water, but not with the higher boiling polymers.

To remove the unsaturated compounds, the distillate was carefully treated with liquid bromine until the reddish brown color was permanent. A subsequent distillation from the water bath removed the high boiling brominated compound. After drying the distillate over anhydrous sodium sulfate and redistilling the pure product was obtained. The yield of the pure product boiling from 48–50° (uncorr. at 750 mm.)<sup>2</sup> was 22.5% of the theoretical amount calculated from gamma chloropropyl acetate.

<sup>1</sup> *Ann. chim.*, [5] 14, 496 (1878).

### III. Properties of Trimethylene Oxide.

Since the properties of trimethylene oxide found by the authors differ decidedly from those reported by Reboul, a tabular comparison is given below:

Physical property.	Authors.	Reboul.
Boiling point.....	47.8° (corr. 760 mm.)	About 50°
Density.....	0.8930	.....
Molecular weight.....	57.9	.....
Index of refraction ( $N_D^{25}$ by Abbé).....	1.3897 $\pm$ 0.0008	.....
Color.....	Colorless	Colorless
Odor.....	Pleasant—aromatic	Penetrating
Solubility in water.....	Completely miscible	Completely miscible
Chemical property.		
Action of bromine.....	None, except after long standing	Vigorous

Since Reboul did not obtain enough of his product to study it further, a few of the chemical properties of trimethylene oxide were compared to those of ethylene oxide. This latter oxide has been thoroughly studied by Wurtz,<sup>1</sup> Grignard,<sup>2</sup> and others. The following table will show the relation of the chemical properties of the two homologs:

Chemical property.	Trimethylene oxide (Authors).	Ethylene oxide.
Action of bromine.....	Very slow	Forms red crystalline compound
Action of $PCl_5$ .....	Vigorous—forms trimethylene chloride	Vigorous—forms ethylene chloride
Action of Grignard reagent	Reacts to synthesize higher alcohols	Reacts to synthesize higher alcohols
Action of $FeCl_3$ solution..	Gives brown ppt.	Gives red-brown ppt.
Action of acetyl chloride..	Vigorous—forms gamma chloropropyl acetate	.....

The physical properties given above demonstrate that a pure monomolecular form of trimethylene oxide was obtained by the authors, but not by Reboul. The chemical properties show that it is an oxide, and further that the impurities in Reboul's product were the unsaturated compounds discussed in Section II. These products were removed by the authors when the crude distillate was treated with bromine. With this definitely established, the excellent analysis of such a volatile product, reported by Reboul, must be attributed to a happy compensation of errors, since one of the main impurities is allyl alcohol, an *isomer* of trimethylene oxide, and the other is allyl chloride. Allyl chloride boils at 47° while the oxide boils at 47.8°, so it is obvious that Reboul could not have freed his product from the chloride by simple distillation, his method of purification. Moreover, the product obtained by the authors,

<sup>1</sup> *Ann. chim.*, [3] 55, 427 (1859).

<sup>2</sup> *Compt. rend.*, 126, 1260 (1903).

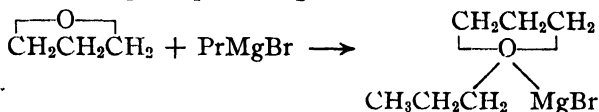


after carefully repeating Reboul's experiment, always possessed three evidences of impurities, namely: reactivity toward liquid bromine, test for chlorine, and a sharp, unpleasant odor.

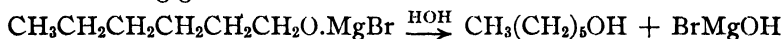
#### IV. Proof of the Atomic Linking Structure.

Trimethylene oxide was treated with phosphorus pentachloride, when a vigorous reaction took place forming trimethylene chloride. The latter was identified by its boiling point, insolubility in cold, concentrated sulfuric acid, and qualitative elementary analysis.

Like ethylene oxide, trimethylene oxide when treated with a magnesium alkyl halide reacts to cleave the ring, giving straight chain compounds. This reaction offers further proof of the structure of trimethylene oxide for, when the oxide is treated with magnesium propyl bromide in ether solution, a reaction takes place producing hexanol-1 as follows:



which on heating gives



The product hexanol-1 was identified by its boiling point, that of its acetate, and the characteristic odor of hexanol-1.

#### V. Experimental Part.

*Preparation of Trimethylene Chlorohydrin by the Chlorohydrin Method.*

**Preparation of the Chlorohydrin by the Action of Hydrogen Chloride upon Trimethylene Glycol.**—Dry hydrogen chloride was prepared by dropping concentrated sulfuric acid upon 37% hydrochloric acid, and drying the evolved gas by passing it through concentrated sulfuric acid. The gas was passed into trimethylene *chlorohydrin* which was kept at a temperature of 100°. At the end of three hours, the product was distilled, the fraction boiling between 150° and 175° containing the chlorohydrin. This was redistilled, and from 130 g. of glycol, 25 g. of trimethylene chlorohydrin boiling at 160–164° were obtained. A large amount of the glycol was recovered unchanged. This method was used by Reboul.

**Action of Sulfur Chloride on Trimethylene Glycol.**—Carius<sup>1</sup> prepared the chlorohydrin of ethylene glycol by the action of sulfur chloride on glycol. The procedure in preparing trimethylene chlorohydrin by this method was as follows:

In a liter flask was placed 250 g. of trimethylene glycol and 450 g. of sulfur chloride. After the mixture had been thoroughly shaken it became warm and there was a lively evolution of sulfur dioxide, while sulfur was precipitated. Without heating, but with occasional shaking, the

<sup>1</sup> *Ann.*, 124, 257 (1862).

lively reaction continued for an hour. When the spontaneous action had ceased, the mixture was heated on the water bath for six hours, using a reflux condenser, and was finally heated for half an hour over the free flame. By this time sulfur dioxide had ceased to be evolved. The cessation of the evolution of sulfur dioxide is adopted as a criterion of the completion of the reaction. The contents of the flask were then cooled and ether added. After removing the ether solution the crystallized sulfur was washed with ether, and the ether extracts combined, and shaken with a saturated solution of sodium carbonate to remove sulfur dioxide. The two liquid layers were then separated and the ether layer dried over anhydrous sodium sulfate. After distilling off the ether, the crude trimethylene chlorohydrin was distilled. The portion boiling  $140-180^{\circ}$  was redistilled and a yield of 160 g. of trimethylene chlorohydrin boiling at  $160-164^{\circ}$  was obtained, this being about 60% of theory. The chlorohydrin is a colorless oil, slightly soluble in water, and has an agreeable odor.

*Preparation of Trimethylene Oxide by the Action of Potassium Hydroxide upon Trimethylene Chlorohydrin.*

The method of Reboul<sup>1</sup> was followed rather closely. A 500 cc. flask was fitted with a dropping funnel, and a thermometer so arranged that the bulb of the thermometer was in the reacting mixture. The side neck was connected with the two U-tubes in series, both immersed in a freezing mixture of hydrochloric acid and ice. In the flask were placed 100 g. of potassium hydroxide and 10 g. of water. The temperature of the mixture was brought to  $130^{\circ}$  where it was maintained throughout the experiment. 50 g. of trimethylene chlorohydrin were added drop by drop through the dropping funnel over a period of 45 minutes. As each drop of the chlorohydrin struck the hot potassium hydroxide, a lively action resulted, and a vapor was evolved which condensed mainly in the first receiver.

**Purification of Trimethylene Oxide.**—After all the chlorohydrin had been added the generating flask was allowed to cool and water was added to dissolve the potassium hydroxide and potassium chloride. The residue was then extracted with ether and the ether extract worked up for high boiling products. The treatment of this residue will be discussed later.

The product which condensed in the receivers was a colorless mobile liquid, soluble in water and having a sharp odor. It was observed that the substance at this stage is very reactive toward liquid bromine. Bromine was added drop by drop to the ice-cold distillate until a permanent bromine color remained. At first the bromine acted instantly and violently, the solution being immediately decolorized. When the permanent

<sup>1</sup> *Ann.*, [5] 14, 496 (1878).

color had been obtained, water was added until the water layer was four times greater in volume than the oily layer. The two layers were then thoroughly mixed by shaking, and the heavy bromide allowed to separate out. This was drawn off and the aqueous layer saturated with potassium carbonate. The solution separated into two layers, the lighter containing the trimethylene oxide. The potassium carbonate solution was drawn off and the crude oxide dried over anhydrous sodium sulfate, and distilled from the water bath. The distillate was redistilled and gave 2 g. of pure trimethylene oxide boiling at 48–49° (uncorr.). It was noticed that the sharp, unpleasant odor of the crude distillate had entirely vanished, and that the odor was now sweet and aromatic.

Several modifications of this method of preparing trimethylene oxide have been tried. An experiment was run in which the temperature of the flask was kept at 160–180°, and the result was a preponderance of unsaturated products and very little trimethylene oxide. The next modification was to use a more dilute solution of potassium hydroxide. Instead of 10 cc. of water to 100 g. of potassium hydroxide, 20 cc. were used. The yield of distillate was very much lessened in this case. Another experiment was run using alcohol as a solvent. Again it was found that mainly unsaturated products were formed. Moreover a considerable quantity of ethyl alcohol distilled over with the low boiling products and the complete separation of the oxide was extremely difficult.

While the chlorohydrin method gave some trimethylene oxide, the quantity was so small that the process could hardly be called a feasible one. In all, seven runs were made, and the average yield was only 5–6% of theory.

*Preparation of Trimethylene Oxide by the Action of Gamma Chloropropyl Acetate upon Potassium Hydroxide.*

**Preparation of Gamma Chloropropyl Acetate.**—A flask having a capacity of 1500 cc. was connected with an upright condenser fitted at the top with a dropping funnel and an outlet tube leading into an absorption apparatus filled with water. In the generating flask was placed 300 g. of trimethylene chlorohydrin. Through the dropping funnel was added slowly 250 g. of acetyl chloride. The hydrogen chloride liberated was absorbed in the absorption train. After all the acetyl chloride had been added the contents of the flask were boiled gently until there was no further evolution of hydrogen chloride. The crude ester was then redistilled, yielding 375 g. of gamma chloropropyl acetate boiling at 160–166°.

**Preparation of Trimethylene Oxide.**—The same apparatus in which the oxide was made by the chlorohydrin method was used in this experiment. 150 g. of solid potassium hydroxide were placed in the 500 cc. generating flask. To this was added 12 cc. of water and the temperature

brought to  $100^{\circ}$ , the bulb of the thermometer being immersed in the potassium hydroxide mixture. Through the dropping funnel was then added slowly, 75 g. of gamma chloropropyl acetate. A lively reaction took place at once, and no further heating was necessary throughout the experiment. The heat evolved by the reaction kept the temperature of the mixture at  $100-110^{\circ}$ . Continued shaking was necessary throughout the experiment to maintain a thorough mixture of the reacting substances. In an hour all the ester had been added, and the mixture was then heated for ten minutes at  $120^{\circ}$ . At this time a marked *odor of the unsaturated compounds*, referred to above, was noticed, and the heating was discontinued. The experiment was duplicated and the products of the two reactions combined. The total weight of the crude distillate from 150 g. of ester was 29 g. It was noticeable that this distillate did not possess nearly so strongly the sharp odor of allyl compounds as did the crude product obtained by the chlorohydrin method, although this odor could still be detected. The whole was placed in a small flask kept cold by immersion in a freezing mixture. Bromine was then added slowly, a much smaller quantity being required to produce the permanent color than in any of the previous experiments. When no more bromine was acted on in the cold, the product was distilled from the water bath and the distillate condensed in a receiver immersed in a freezing mixture. The distillate was colored slightly yellow from the excess bromine. Anhydrous sodium sulfate was added and the products was allowed to stand for 24 hours in a glass-stoppered bottle. At the end of that time the color had disappeared. The crude trimethylene oxide was distilled, giving 14 g. of pure trimethylene oxide boiling at  $48-50^{\circ}$  (uncorr.). This is 22.5% of the amount predicted by theory.

*Study of the Chemical Properties of Trimethylene Oxide.*

**Synthesis of Hexanol-1.**—Magnesium propyl bromide was prepared by the action of 4.3 g. of magnesium ribbon upon 24 g. of propyl bromide in absolute ether. To this was added 10 g. of trimethylene oxide in 25 cc. of absolute ether. This was added slowly, to prevent too rapid reaction. When all had been added, the mixture was refluxed for an hour, using an upright condenser. The water was then drawn from the condenser and the ether evaporated. As the last traces of ether were evaporated the mass became porous and metallic looking. Suddenly a violent reaction took place, evolving a good deal of heat and leaving the residue somewhat charred and in the form of a hard cake. Water was then added to the cooled mixture, causing a slight heating. When the product was distilled with steam, about 2 cc. of an oil were obtained which had an odor much like that of hexanol-1. The volume was not great enough, however, to permit of purification by redistillation.

In order to determine a means of preventing this violent decomposi-

tion, a modification of this method was tried. Half the above quantities were used and the magnesium propyl bromide was prepared in the same manner as before. To the ether solution was added 5 g. of trimethylene oxide in 10 cc. of ether, and the mixture refluxed as before. Instead of distilling off the ether at this point, 100 cc. of dry benzene were added to the mixture, and the ether evaporated from this leaving the benzene as the solvent for the reacting substances. While the ether was being evaporated a thermometer was suspended in the upright condenser. When the temperature of the distilling vapors had reached  $70^{\circ}$ , the mixture was refluxed under the water cooler for four hours. The complex which had been precipitated as a gray solid, on the addition of the trimethylene oxide, became pasty under this treatment. No change of color, however, was noticeable. The mixture was now cooled and water added, without visible evidence of heat effect. As the gray mass went into solution a white precipitate formed at the bottom of the flask, and the liquid portion separated into two layers. The precipitate was dissolved in 30% sulfuric acid and the mixture distilled with steam. The distillate collected in two layers, and after separation, the oil was dried over anhydrous sodium sulfate and redistilled. After the benzene had passed over, 5 cc. of a liquid distilling constant at  $155^{\circ}$  were obtained. This was identified as hexanol-1.

**Action of Phosphorus Pentachloride.**—When trimethylene oxide was treated with phosphorus pentachloride, a violent reaction took place and an oil insoluble in water and in cold concentrated sulfuric acid was formed. The liquid was identical in its properties with trimethylene chloride.

**Action of Acetyl Chloride.**—Acetyl chloride reacts violently with trimethylene oxide to form gamma chloropropyl acetate.

*Physical Properties of Trimethylene Oxide.*

**Determination of the Boiling Point.**—The boiling point of trimethylene oxide was determined by the equilibrium method. The following table shows the readings of the thermometer, together with those readings corrected for emergent stem, for calibration and for variation of the atmospheric pressure from 760 mm.:

Readings.....	47.35	47.45	47.40	47.50
B. p. 760 mm.....	47.77	47.87	47.82	47.92

**Determination of the Specific Gravity.**—The specific gravity of trimethylene oxide was determined in an ordinary specific gravity bottle. The determinations were made at  $25^{\circ}$ . Densities are compared to water at  $4^{\circ}$ .

Wt. bulb with oxide, g.	Wt. bulb empty, g.	Volume of bulb, cc.	Wt. of oxide, g.	Sp. gr. of oxide.
10.6760	6.0086	5.2272	4.6674	0.8930
10.6770	6.0086	5.2272	4.6684	0.8931

**Determination of the Index of Refraction.**—The index of refraction of trimethylene oxide was determined by the Abbé refractometer using ordinary (white) light. The following readings were taken:

$n_D^{20}$  . . . . 1.3900, 1.3895, 1.3899, 1.3899, 1.3897, 1.3892, 1.3901, 1.3895, 1.3898, 1.3899.

**Determination of the Molecular Weight.**—The molecular weight of trimethylene oxide was determined by the method of Victor Meyer. Three determinations were made with the following results: 61.5; 56.8; 55.5. The calculated molecular weight is 58.

**Residues from the Preparation of Trimethylene Oxide (Chlorohydrin Method).**—After the trimethylene oxide had been driven from the generating flask, the residues were cooled and the water solutions extracted with ether. The ether solution was dried over anhydrous sodium sulfate, and the ether distilled over. The residue was subjected to fractional distillation. A considerable quantity of the liquid distilled over below  $100^\circ$ . This portion was treated with bromine and found to add that substance quantitatively. From  $100$  to  $150^\circ$  little distilled over, but from  $150$  to  $190^\circ$  there was an increased quantity of distillate. It was this portion that Reboul considered to be the unchanged chlorohydrin. But it was found that this fraction also reacted vigorously and completely with bromine to form heavy oils, while the chlorohydrin under similar conditions will not react at all. From  $200^\circ$  under ordinary pressure to  $270^\circ$  under 30 mm. several fractions were obtained, all of which formed heavy bromides with bromine. The latter fractions were viscous oils which seemed to have minute crystals in the liquid. However, they did not crystallize further on standing for three months.

URBANA, ILL.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF CORNELL UNIVERSITY.]

## THE NITRATION PRODUCTS OF PHENOLTETRACHLOROPHTHALEIN AND SOME OF THEIR DERIVATIVES.

BY W. R. ORNDORFF AND J. J. KENNEDY.

Received September 8, 1916.

The investigation of the nitration products of phenoltetrachlorophthalein and their derivatives was undertaken to study the effect of introducing negative groups into the phthalein molecule.

The phenol used in this investigation was a pure crystallized product. This was distilled, the first fraction being rejected, and only that distilling between  $180^\circ$  and  $181^\circ$  was used. This product was perfectly colorless and melted sharply at  $42^\circ$ . Commercial tetrachlorophthalic acid was purified by the method described by Delbridge.<sup>1</sup> The purity of the acid

<sup>1</sup> *Am. Chem. J.*, 41, 414 (1909).

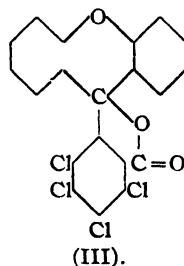
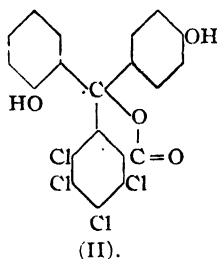
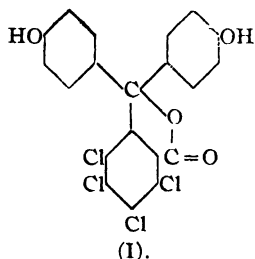
used was checked by determining its molecular weight by titration<sup>1</sup> with standard alkali.

**Phenoltetrachlorophthalein.**—This compound was made by the method of Orndorff and Black,<sup>2</sup> the only difference being that tetrachlorophthalic acid was used instead of the corresponding amount of tetrachlorophthalic anhydride. The yield of the phthalein was the same and the same amount of tetrachlorofluoran was formed. The pure phenoltetrachlorophthalein<sup>3</sup> was found to melt<sup>4</sup> sharply at 316–317°, with decomposition. The product, dried in an electric oven<sup>5</sup> at 120°, gave the following results on analysis:<sup>6</sup>

Subst., I, 0.2249; II, 0.2021; cc. 0.1 *N* AgNO<sub>3</sub>, I, 19.78; II, 17.71.

Calc. for C<sub>20</sub>H<sub>10</sub>Cl<sub>4</sub>O<sub>4</sub>: Cl, 31.11%. Found: I, 31.19; II, 31.07.

**Phenoltetrachlorophthalein Dibenzoate.**—This compound was not made by Orndorff and Black. It was prepared to determine if the phenoltetrachlorophthalein was not a mixture of two isomers. According to theory, three products are possible in the condensation of phenol with tetrachlorophthalic acid.



The compound represented by Formula III is tetrachlorofluoran, easily separated from the phthalein, owing to its insolubility in aqueous alkali. The greater amount of the product formed probably has the structure represented by Formula I in which the methane carbon atom is in the para position to each of the hydroxyl groups. However, the compound, represented by Formula II, in which one hydroxyl is ortho and the other para to the methane carbon atom, presents another possibility. If phenoltetrachlorophthalein is a mixture of these two phthaleins, then two dibenzoates should be formed. With this idea in view, the

<sup>1</sup> *Am. Chem. J.*, 41, 399 (1909).

<sup>2</sup> *Ibid.*, 41, 360 (1909).

<sup>3</sup> Phenoltetrachlorophthalein is described by Orndorff and Black as not melting at 300°.

<sup>4</sup> All melting points described in this article are uncorrected and were determined with carefully standardized thermometers using an electrically heated Thiele apparatus.

<sup>5</sup> *Am. Chem. J.*, 48, 477 (1912).

<sup>6</sup> All the chlorine determinations were made by the lime method. *Am. Chem. J.*, 41, 393 (1909). International atomic weights for 1916 are used in this article.

benzoyl derivative of phenoltetrachlorophthalein was made and carefully studied. Ten grams of phenoltetrachlorophthalein were heated to boiling with 70 g. of pure benzoyl chloride when all the phthalein went into solution. The boiling was continued for ten minutes and the contents of the flask poured into alcohol. The benzoate, after repeated washing with boiling water, was obtained in a nearly colorless, amorphous condition. It was then boiled with 95% alcohol, to remove the last traces of benzoyl chloride. The yield was practically quantitative, 98% of the calculated amount being obtained. The benzoate was crystallized several times from a *boiling* mixture of acetone and ethyl alcohol and obtained as a colorless, crystalline product, melting at  $213^{\circ}$ . Analyses showed that this product, was the pure anhydrous dibenzoate. On heating for an hour at  $120^{\circ}$  there was no loss in weight.

Subst., I, 0.2052; II, 0.2304; cc. 0.1  $N$   $AgNO_3$ , I, 12.37; II, 13.85.

Calc. for  $C_{24}H_{18}O_6Cl_4$ : Cl, 21.36%. Found: I, 21.38; II, 21.31.

Some of the product melting at  $213^{\circ}$  was then recrystallized from a mixture of acetone and ethyl alcohol *in the cold*. It now appeared in the form of flocks melting at about  $165^{\circ}$ . Another portion of the anhydrous material recrystallized slowly from benzene in the cold was obtained in white flocks, melting at about  $155^{\circ}$ . The compound from benzene lost a molecule of water,

Subst., I, 0.3144; II, 0.4235, loss (water) at  $130^{\circ}$ ; I, 0.0074; II, 0.0102.

Calc. for  $C_{24}H_{18}O_6Cl_4$ :  $H_2O$ , 2.64%. Found: I, 2.35; II, 2.40,

and no benzene could be detected in the vapors given off. This molecule of water is not lost when the product is placed in an evacuated desiccator over phosphorus pentoxide for several days, and is probably not water of crystallization (page 2500). The product from acetone, however, lost only about one-third of a molecule of water, showing that it was undoubtedly a mixture of the anhydrous material, and the hydrate. After water was driven off both products melted at  $213^{\circ}$  and analyses showed them to be the pure anhydrous dibenzoate.

The dibenzoate of phenoltetrachlorophthalein is readily soluble in acetone, benzene, and ethyl acetate; nearly insoluble in ethyl alcohol, methyl alcohol and ether. It is insoluble in 10% alkali in the cold. On warming, partial saponification slowly takes place.

As the entire amount of the anhydrous dibenzoate had a constant melting point of  $213^{\circ}$ , and in the course of fractional crystallization no indication of an isomer presented itself, it is highly probable that phenoltetrachlorophthalein is not a mixture of two isomers and is correctly represented by Formula I (page 2487).

As Orndorff and Hitch<sup>1</sup> had found that tetrachlorofluorescein gave only a monobenzoate by the Baumann-Schotten reaction, an attempt was made

<sup>1</sup> *J. Am. Chem. Soc.*, 36, 692 (1914).



to obtain the monobenzoate of phenoltetrachlorophthalein, by this method using 10 g. of phenoltetrachlorophthalein, 9 g. potassium hydroxide and 10 g. of benzoyl chloride. The product after purification was found to melt at  $213^{\circ}$  and an analysis showed conclusively that it was the dibenzoate.

Subst., 0.2456, cc. 0.1  $N$   $\text{AgNO}_3$ , 14.75.

Calc. for  $\text{C}_{34}\text{H}_{18}\text{O}_6\text{Cl}_4$ : Cl, 21.36. Found: 21.30.

**Dinitrophenoltetrachlorophthalein** was made as follows: Ninety-six grams of phenoltetrachlorophthalein were heated with a mixture of 1500 g. of glacial acetic acid and 147 g. of sulfuric acid (sp. gr. 1.84) about one hour at  $80^{\circ}$ . The mixture was then cooled to  $20^{\circ}$ , and 49 g. of nitric acid (sp. gr. 1.42) gradually added. The temperature was raised to  $50^{\circ}$  by immersing the flask in hot water, complete solution of the phthalein resulting. Extreme care had to be taken at this point not to allow the temperature to rise above  $50^{\circ}$ , otherwise higher nitration products were formed in sufficient quantity to make the purification of the dinitro compound extremely difficult. The solution was then cooled to room temperature and stirred for 24 hours until no unchanged phenoltetrachlorophthalein could be detected. The nitration product, which crystallized out, was filtered off and washed several times with small amounts of alcohol to remove impurities which imparted to the alcohol an orange color. The yellow dinitro product was then fractionally crystallized from acetone. All fractions finally showed a constant melting point of  $240^{\circ}$ . A small portion crystallized from glacial acetic acid also melted sharply at  $240^{\circ}$ . By adding water to the original nitrating solution, a small amount of dinitro product separated as a light yellow flocculent precipitate. This was purified as described above. The yield of the purified product was about 80%. Fractions crystallized from both acetone and glacial acetic acid lost no weight on heating. The material dried at  $130^{\circ}$ , gave the following results on analysis:<sup>1</sup>

Subst., I, 0.2672; II, 0.2135; cc. 0.1  $N$   $\text{AgNO}_3$ ; I, 19.57; II, 15.70.

Calc. for  $\text{C}_{20}\text{H}_8\text{Cl}_4\text{O}_8\text{N}_2$ : Cl, 25.98%. Found: I, 25.97; II, 26.08.

Subst., I, 0.3494; II, 0.3587; cc. 0.1  $N$   $\text{HCl}$ ; I, 13.00; II, 13.25.

Calc. for  $\text{C}_{20}\text{H}_8\text{Cl}_4\text{O}_8\text{N}_2$ : N, 5.13%. Found: I, 5.21; II, 5.15.

Dinitrophenoltetrachlorophthalein is light yellow in color and dissolves in caustic alkalis and alkali carbonates, with a light yellow color, more concentrated solutions having an orange color. It is insoluble in alkali bicarbonates. It is somewhat soluble in glacial acetic acid and ethyl acetate, more readily soluble in acetone. It is comparatively insoluble in ether, ethyl alcohol, methyl alcohol, and benzene.

An attempt was made to obtain a hydrate, or a carbinol acid of the dinitro

<sup>1</sup> In this work, all determinations of nitrogen were made by first reducing the nitro compounds by means of zinc dust and concentrated sulfuric acid, and then proceeding as in the Kjeldahl-Gunning method.

tro product by dissolving it in potassium hydroxide solution and precipitating with hydrochloric acid. On heating, the product lost no weight even at  $200^{\circ}$  and an analysis showed that it was the anhydrous dinitrophenoltetrachlorophthalein.

Subst., 0.2357; cc. 0.1  $N$   $AgNO_3$ , 17.19.

Calc. for  $C_{20}H_8Cl_4O_8N_2$ : Cl, 25.98. Found: 25.86.

All attempts to prepare dinitrophenoltetrachlorophthalein by the condensation of orthonitrophenol and tetrachlorophthalic anhydride, using such condensing agents as sulfuric acid (sp. gr. 1.84), fuming sulfuric acid (containing 15% of free sulfur trioxide) and freshly fused zinc chloride, were without success.

**Action of Dry Ammonia on Dinitrophenoltetrachlorophthalein.**—When treated with dry ammonia, the dinitro product gradually changed from light yellow to dark brown. Three molecules of ammonia were absorbed in a few hours. It, however, continued to gain weight slowly for four days when it absorbed four molecules of ammonia. When the salt was exposed to the air, the ammonia was gradually given off and the product returned to approximately the original weight. The small amount of ammonia which remained was readily driven off by heating at  $80^{\circ}$ .

Subst., I, 0.5182; II, 0.7526; gain in wt., I, 0.0625; II, 0.0942.

Calc. for  $C_{20}H_8Cl_4O_8N_2 \cdot 4NH_3$ :  $NH_3$ , 11.10%. Found: I, 10.76; II, 11.12.

**Dinitrophenoltetrachlorophthalein Dibenzoate.**—Five grams of dinitrophenoltetrachlorophthalein were boiled with 35 g. of benzoyl chloride for a half hour. The dark brown solution was poured into ethyl alcohol when the benzoate separated as a dark brown oil. After considerable shaking, the oil solidified. It was recrystallized from benzene by the addition of ethyl alcohol, and obtained colorless with a sharp melting point of  $205^{\circ}$ . A fraction crystallized from acetone showed no change in melting point. This product was the hydrate (page 2500). Loss in weight determinations at  $120^{\circ}$  were made with fractions crystallized from a mixture of benzene and ethyl alcohol and also from acetone. In each case the vapors from the drying tube were conducted into a wash bottle containing water, but neither acetone nor ethyl alcohol could be detected in the water.

Subst., I, 0.9985; II, 0.4729; loss (water) at  $120^{\circ}$ , I, 0.0240; II, 0.0113.

Calc. for  $C_{24}H_{16}Cl_4O_{10}N_2 \cdot H_2O$ , 2.33%. Found: I, 2.40; II, 2.39.

The molecule of water is not lost on standing for days in an evacuated desiccator over phosphorus pentoxide. The product is, therefore, a hydrate. The anhydrous dibenzoate also melted sharply at  $205^{\circ}$  and gave the following results on analysis:

Subst., I, 0.2326; II, 0.2286; cc. 0.1  $N$   $AgNO_3$ ; I, 12.31; II, 12.03.

Calc. for  $C_{24}H_{16}Cl_4O_{10}N_2$ : Cl, 18.81. Found: I, 18.77; II, 18.66.

Dinitrophenoltetrachlorophthalein dibenzoate is readily soluble in benzene, acetone and ethyl acetate. It is comparatively insoluble in methyl

alcohol, ethyl alcohol, and ether. In hot 10% sodium hydroxide solution, the product is slowly, but only partially, saponified, the solution becoming orange in color.

By benzoylating dinitrophenoltetrachlorophthalein according to the Baumann-Schotten reaction, the same dibenzoate was obtained. The material melted sharply at  $205^{\circ}$  and, after drying to constant weight at  $120^{\circ}$ , gave the following result on analysis:

Subst., 0.2646, cc. 0.1  $N$   $\text{AgNO}_3$ , 14.18.

Calc. for  $\text{C}_{24}\text{H}_{12}\text{Cl}_4\text{O}_{10}\text{N}_2$ : Cl, 18.81%. Found: 19.01.

Hence, dinitrophenoltetrachlorophthalein, like phenoltetrachlorophthalein, does not give a monobenzoate by the Baumann-Schotten reaction.

**Dinitrophenoltetrachlorophthalein Diacetate.**—Ten grams of dinitrophenoltetrachlorophthalein were boiled for half an hour with 70 g. of pure acetic anhydride. The acetate was then extracted a few times with small amounts of boiling alcohol, in which it is practically insoluble. After crystallizing from benzene, pale yellow crystals were obtained melting at  $136^{\circ}$ . The air-dried product lost no weight on standing for several days in an evacuated desiccator over phosphorus pentoxide. The following results were obtained on analysis:

Subst., I, 0.2684; II, 0.2519; cc. 0.1  $N$   $\text{AgNO}_3$ ; I, 16.24; II, 15.25.

Calc. for  $\text{C}_{24}\text{H}_{12}\text{Cl}_4\text{O}_{10}\text{N}_2$ : Cl, 22.52%; for  $\text{C}_{24}\text{H}_{12}\text{Cl}_4\text{O}_{10}\text{N}_2 \cdot 2\text{H}_2\text{O}$ : Cl, 21.30%. Found: I, 21.46; II, 21.47.

On heating some of the air-dried substance in the electric oven to constant weight at  $105^{\circ}$ , one molecule of water is lost.

Subst., I, 0.4131; II, 0.4188; loss (water); I, 0.0114; II, 0.0120.

Calc. for  $\text{C}_{24}\text{H}_{12}\text{Cl}_4\text{O}_{10}\text{N}_2$ :  $\text{H}_2\text{O}$ , 2.78%. Found: I, 2.76; II, 2.86.

When the temperature was raised to  $140^{\circ}$ , the product melted and after heating five hours another molecule of water was lost.

Subst., I, 0.4131; II, 0.4188; loss (water); I, 0.0230; II, 0.0234.

Calc. for  $\text{C}_{24}\text{H}_{12}\text{Cl}_4\text{O}_{10}\text{N}_2$ :  $2\text{H}_2\text{O}$ , 5.41%. Found: I, 5.56; II, 5.59.

In the above determinations no benzene could be detected in the vapors from the material. The anhydrous material thus obtained gave the following results on analysis:

Subst., I, 0.3707; II, 0.4206; cc. 0.1  $N$   $\text{AgNO}_3$ ; I, 23.45; II, 26.58.

Calc. for  $\text{C}_{24}\text{H}_{12}\text{Cl}_4\text{O}_{10}\text{N}_2$ : Cl, 22.52%. Found: I, 22.43; II, 22.41.

Some of the air-dried material which dissolved readily in benzene giving a colorless solution, was then dissolved in acetone and the solution was bright yellow in color. A fraction crystallized from acetone remained constant in weight when kept for several days in a vacuum over phosphorus pentoxide. Moreover, on heating in the electric oven at  $105^{\circ}$  for two hours, there was no loss in weight. When, however, the temperature was raised to  $140^{\circ}$ , the product melted and after heating five hours

it became constant in weight, one molecule of water being lost. Acetone could not be detected in the vapors given off from the material. The substance then gave, on analysis, results for the anhydrous diacetate. Dinitrophenoltetrachlorophthalein diacetate, therefore, crystallizes from benzene with two molecules of water, one molecule being held more firmly than the other. It crystallizes from acetone with only one molecule of water.

Dinitrophenoltetrachlorophthalein diacetate is readily soluble in benzene, acetone and ethyl acetate, but almost insoluble in methyl and ethyl alcohols. It does not dissolve in cold 10% sodium hydroxide solution, but on warming partial saponification takes place, the solution becoming deep orange in color.

**Monobromodinitrophenoltetrachlorophthalein.**—Ten grams of dinitrophenoltetrachlorophthalein were suspended in 200 cc. of glacial acetic acid, and 6 g. of bromine in 25 cc. of glacial acetic acid added dropwise. The dinitro product did not dissolve on boiling the solution. Six grams more of bromine were then added, and the solution heated till the dinitro product was completely dissolved. The clear solution was poured into a large excess of water and the yellow precipitate crystallized from a mixture of acetone and ethyl alcohol. After recrystallizing a few times all fractions showed a sharp melting point of 220–221°. A fraction crystallized from glacial acetic acid showed no variation in the melting point.

The chlorine and bromine determinations on this compound were made by the method already described.<sup>1</sup> After heating, the contents of the tube were dissolved in *dilute* nitric acid, care being taken to keep the solution cold and to avoid large excess of nitric acid. (When these precautions were not taken, a yellow filtrate was always obtained on filtering off the carbon. This was due to free bromine which would be lost and cause low results in the halogen content.)

The following results were obtained on the material dried at 120°:

	Substance. Gram.	Silver halides. Gram.	Tenth-normal silver nitrate.	Chlorine. Per cent.	Bromine. Per cent.
I.....	0.2243	0.2740	18.00 cc.	22.77	12.81
II.....	0.2441	0.2969	19.56 cc.	23.01	12.17
Calculated for $C_{20}H_7BrCl_4N_2O_8$ .....				22.70	12.79

Subst., I, 0.3414; II, 0.3778; cc. 0.1 N HCl; I, 11.00; II, 11.89.

Calc. for  $C_{20}H_7BrCl_4N_2O_8$ : N, 4.48%. Found: I, 4.51; II, 4.41.

The monobromodinitrophenoltetrachlorophthalein was obtained as a bright yellow, crystalline compound, showing slightly more color than the dinitrophenoltetrachlorophthalein, and differing from the latter in its greater solubility in the ordinary solvents. The compound is readily soluble in caustic alkalies and alkali carbonates with a deep orange color. It is insoluble in alkali bicarbonates.

<sup>1</sup> *Am. Chem. J.*, 41, 380 (1909).

**Action of Dry Ammonia on Monobromodinitrophenoltetrachlorophthalein.**—When placed in dry ammonia gas, this compound gradually absorbed five molecules of ammonia and came to constant weight in two days, changing in color from a bright yellow to a dark brown.

Subst., 0.5652; gain in wt., 0.0741.

Calc. for  $C_{20}H_7BrCl_4N_2O_8 \cdot 5NH_3$ :  $NH_3$ , 11.99. Found: 11.59.

When this salt was placed in a tube and a current of dry air passed over it, three molecules of ammonia were lost within an hour. The diammonium salt is not stable and gradually loses ammonia on standing in a desiccator over calcium chloride, at the end of seven days less than one molecule of ammonia remaining. A small amount of ammonia is held indefinitely at room temperature. When, however, this product is heated to  $100^\circ$  for an hour, all ammonia is driven off, and the compound returns to its original color and weight.

**Dibromodinitrophenoltetrachlorophthalein** was obtained as follows: Ten grams of dinitrophenoltetrachlorophthalein were suspended in 200 cc. of glacial acetic acid, and 15 g. of bromine in 25 cc. of glacial acetic acid added. The solution was heated to boiling when the dinitro compound dissolved completely, and at the end of two hours a bright yellow precipitate began to separate from the boiling solution. It was then filtered and the product crystallized from acetone. After recrystallizing a few times, a small amount of a compound with a lower melting point, undoubtedly the monobromo compound, was separated. All fractions then melted sharply at  $271$ – $272^\circ$ , with decomposition. A fraction from glacial acetic acid also had the same melting point. The following results were obtained on analysis:

Subst. Gram.	Silver halides. Gram.	Tenth-normal silver nitrate.	Chlorine. Per cent.	Bromine. Per cent.
0.2787	0.3684	23.31 cc.	19.85	22.11

In the above determination the mixture of silver halides was treated with chlorine and the following results obtained:<sup>1</sup>

Subst. Gram.	Silver halides. Gram.	Decrease. Gram.	Chlorine. Per cent.	Bromine. Per cent.
0.2787	0.3684	0.0340	19.95	21.93
Calculated for $C_{20}H_6Br_2Cl_4N_2O_8$ .....			20.15	22.71

Analysis of the compound for nitrogen gave the following results:

Subst., I, 0.4161; II, 0.3800; cc. 0.1 *N* HCl; I, 11.62; II, 10.33.

Calc. for  $C_{20}H_6Br_2Cl_4N_2O_8$ : N, 3.98. Found: I, 3.91; II, 3.81.

The dibromo compound differs from the monobromo product in its greater insolubility in acetone, glacial acetic acid, benzene, ethyl and methyl alcohols. It is soluble in acetone; less soluble in glacial acetic acid, and only sparingly soluble in methyl and ethyl alcohols and in

<sup>1</sup> *J. Am. Chem. Soc.*, 36, 702 (1914).

benzene. It dissolves in caustic alkalis and alkali carbonates, with a reddish orange color. It is insoluble in alkali bicarbonates.

**Action of Dry Ammonia on Dibromodinitrophenoltetrachlorophthalein.**—This product absorbed five molecules of ammonia in 20 hours and changed from a bright yellow to a bright orange color.

Subst., I, 0.5286; II, 5294; gain in wt.; I, 0.0611; II, 0.0618.

Calc. for  $C_{20}H_6Br_2Cl_4N_2O_8 \cdot 5NH_3$ :  $NH_3$ , 10.97%. Found: I, 10.36; II, 10.45.

When dry air was passed over this salt at room temperature, three molecules of ammonia were lost very readily, the product changing in color from a bright orange to a dark orange color. An analysis made by heating the salt to  $125^\circ$  and collecting the ammonia in standard tenth-normal hydrochloric acid solution, showed that the product was the diammonium salt.

Subst., 0.5530; cc. 0.1 *N* HCl, 13.85.

Calc. for  $C_{20}H_6Br_2Cl_4N_2O_8 \cdot 2NH_3$ :  $NH_3$ , 4.61%. Found: 4.20.

When all of the ammonia was driven off, the product returned to the original weight and color of the dibromo compound. The diammonium salt is not stable in the air, but slowly loses ammonia and takes up moisture. In a desiccator over fused calcium chloride, the ammonia is slowly lost, less than one molecule remaining after standing ten days.

**Diaminophenoltetrachlorophthalein.**—Ten grams of dinitrophenoltetrachlorophthalein were heated with a solution of 100 cc. of absolute alcohol saturated with dry hydrochloric acid gas and 50 g. of crystallized stannous chloride on the water bath for a half hour. Complete reduction of the dinitro compound took place and a copious white precipitate of the double tin salt of the diamino compound separated. This was filtered off, washed with concentrated hydrochloric acid and dissolved in hot water. The tin was removed by passing hydrogen sulfide into the acidified solution and the colorless filtrate carefully neutralized with ammonia. The free base separated as a coffee-brown crystalline powder. It was recrystallized from ethyl alcohol by the addition of water and after crystallizing a few times, obtained as bright orange-colored crystals. The following results were obtained on analysis:

Subst., I, 0.2240; II, 0.2873; cc. 0.1 *N*  $AgNO_3$ ; I, 18.50; II, 23.68.

Subst., 0.4979; cc. 0.1 *N* HCl, 19.87.

Calc. for  $C_{20}H_{12}Cl_4N_2O_4$ : N, 5.77%; Cl, 29.19%. Found: N, 5.59; Cl, I, 29.28; II, 29.23.

The diaminophenoltetrachlorophthalein does not melt even when heated to  $335^\circ$ . It turns dark, however, showing decomposition. It dissolves in caustic alkalis, alkali carbonates, and in ammonia, with a prussian blue color. These alkaline solutions, however, are unstable, and on long standing the color gradually disappears. The diamino compound does not dissolve in alkali bicarbonates. It dissolves in concentrated sulfuric acid with a pink color. On warming slightly no change

takes place, but on adding a small amount of water, the solution becomes colorless. In concentrated hydrochloric acid, the bright orange crystals of the diamino compound are changed to those of the colorless hydrochloride.

**Diaminophenoltetrachlorophthalein Dihydrochloride.**—Two grams of the pure diamino compound were boiled for an hour with 200 cc. of hydrochloric acid solution (1 : 1). The colorless hydrochloride was then filtered off, washed with water containing hydrochloric acid, and dried in the air for one week. The following result was obtained on analysis of the air-dried product:

Subst., 0.1452; cc. 0.1 *N* AgNO<sub>3</sub>, 15.50.

Calc. for C<sub>20</sub>H<sub>12</sub>Cl<sub>4</sub>N<sub>2</sub>O<sub>4</sub>·2HCl: Cl, 38.07%. Found: 37.86.

The hydrochloric acid was determined by weighing portions of the air-dried material into Erlenmeyer flasks, adding water, and heating until the hydrochloride was decomposed. The insoluble free base was filtered off, and the acid in the filtrate determined by titration with standard alkali, enough of the diaminophenoltetrachlorophthalein remaining in solution to act as indicator.

Subst., I, 0.4956; II, 0.3089; cc. 0.1 *N* HCl, I, 17.40; II, 10.94.

Calc. for C<sub>20</sub>H<sub>12</sub>Cl<sub>4</sub>N<sub>2</sub>O<sub>4</sub>·2HCl: HCl, 13.05%. Found: I, 12.80; II, 12.92.

The diaminophenoltetrachlorophthalein dihydrochloride is soluble in water but insoluble in water containing hydrochloric acid. When its aqueous solution is boiled, the salt is decomposed and the free diaminophenoltetrachlorophthalein crystallizes from the solution.

**Tetranitrophenoltetrachlorophthalein.**—This compound was made as follows: 60 g. of phenoltetrachlorophthalein were heated on the water bath to a temperature of 80–90° about an hour with 720 g. of sulfuric acid (sp. gr. 1.84). Complete solution took place and when a small portion was withdrawn and poured into water there was no precipitation of the phthalein, showing that complete conversion into the sulfonic acid had taken place. The solution was cooled to 0° and a mixture of 70 g. of nitric acid (sp. gr. 1.42) and 70 g. of sulfuric acid (sp. gr. 1.84) slowly added and the solution mechanically stirred for an hour, the temperature being allowed to rise to 35°. At the end of this time, the solution became cloudy and the yellow nitration product began to separate out. The nitration mixture was allowed to stand overnight and added to a large amount of water. The crude product was light yellow in color and the yield was about 80%. It was crystallized several times from acetone and obtained in the form of very fine needles, melting at 289–290°. Fractions crystallized from both nitrobenzene and glacial acetic acid showed no change in the melting point. Some of the product, crystallized from acetone, was dried in the air and a weighed amount placed in an evacuated desiccator over phosphorus pentoxide. It stood several

days, and a small amount of mechanically-held solvent was lost. When this material was heated in a drying tube at  $185^{\circ}$ , two molecules of water were given off.

Subst., I, 0.4180; II, 0.6417; loss (water); I, 0.0211; II, 0.0344.

Calc. for  $C_{20}H_6Cl_4O_{12}N_4 \cdot 2H_2O$ :  $H_2O$ , 5.36%. Found: I, 5.05; II, 5.36.

In order to prove that no acetone was given off, the vapors from the drying tube were passed into an absorption bottle containing water. No acetone could be detected by the iodoform reaction.

The anhydrous material gave the following results on analysis:

Subst., I, 0.2464; II, 0.2600; cc. 0.1 *N*  $AgNO_3$ ; I, 15.57; II, 16.34.

Subst., 0.3333; cc. 0.1 *N*  $HCl$ , 21.27.

Calc. for  $C_{20}H_6Cl_4O_{12}N_4$ : N, 8.81%; Cl, 22.51%. Found: N, 8.94; and Cl, I, 22.41; II, 22.28.

The tetranitrophenoltetrachlorophthalein differs from the dinitrophenoltetrachlorophthalein in its greater insolubility in the ordinary organic solvents. It is comparatively soluble in acetone; soluble in acetic acid to the extent of less than one-half per cent., and practically insoluble in methyl and ethyl alcohols and in benzene. It dissolves in caustic alkalies and alkali carbonates with a clear yellow color, more concentrated solutions having an orange color. Unlike the dinitrophenoltetrachlorophthalein, it dissolves in alkali bicarbonates with a yellow color. This behavior shows the stronger acid properties of the tetranitro compound.

**Action of Dry Ammonia on Tetranitrophenoltetrachlorophthalein.**—The anhydrous compound was treated with dry ammonia gas. More than two molecules of ammonia were absorbed in less than one minute, and the product changed from yellow to a deep orange color. At the end of an hour four molecules of ammonia were absorbed, but the product continued to absorb ammonia very slowly for two days, increased very markedly in volume, and finally absorbed five molecules of ammonia.

Subst., I, 0.3975; II, 0.4540; gain in wt.; I, 0.0518; II, 0.0594.

Calc. for  $C_{20}H_6Cl_4O_{12}N_4 \cdot 5NH_3$ :  $NH_3$ , 11.81%. Found: I, 11.53; II, 11.57.

The salt was placed in a tube and a current of *dry* air passed over it, previous work having shown that the salt was quite hygroscopic, absorbing moisture from the air and at the same time losing ammonia. In the course of a few hours, almost three of the five molecules of ammonia were lost. It was then placed in a vacuum over phosphorus pentoxide for several days. No weight was lost after the first day. This compound, according to the calculations from the amount of ammonia still held, was the diammonium salt. This was further verified by heating it at  $150^{\circ}$  and collecting the ammonia in an absorption bottle, containing standard hydrochloric acid solution. The excess hydrochloric acid was then titrated with standard ammonium hydroxide, using methyl red as indicator.



Subst., 0.3975, wt. of salt, 0.4176; cc. 0.1 *N* HCl, 11.80.

Calc. for  $C_{20}H_{16}Cl_4O_{12}N_4 \cdot 2NH_3$ :  $NH_3$ , 5.09%. Found: 4.81.

After heating, the product returned to the original weight and color of the tetranitro compound.

**Tetranitrophenoltetrachlorophthalein Dibenzoate.**—This compound was prepared in the same way as the corresponding dinitro product (page 2490). The yield of the dibenzoate was practically quantitative, and the product appeared as very fine, almost colorless crystals. It was recrystallized from nitrobenzene by the addition of ethyl alcohol. On heating the air-dried product to  $135^\circ$ , no loss in weight ensued. The following results were obtained on analysis:

Subst., I, 0.2269; II, 0.2805; cc. 0.1 *N*  $AgNO_3$ ; I, 10.69; II, 13.21.

Calc. for  $C_{34}H_{14}Cl_4O_{14}N_4$ : Cl, 16.81%. Found: I, 16.71; II, 16.70.

The tetranitrophenoltetrachlorophthalein dibenzoate melts with decomposition at  $285^\circ$ . It dissolves readily in hot nitrobenzene, but is practically insoluble in methyl and ethyl alcohols, ethyl acetate, acetone, ether, benzene, and xylene. It is insoluble in cold dilute sodium hydroxide. On boiling, partial saponification takes place, the supernatant liquid becoming orange in color.

An attempt was made to prepare a benzoate of tetranitrophenoltetrachlorophthalein by means of the Baumann-Schotten reaction. Instead of the expected benzoyl derivative, a potassium salt of tetranitrophenoltetrachlorophthalein was obtained.

**Tetranitrophenoltetrachlorophthalein Diacetate.**—This compound was prepared in the same way as the corresponding dinitro product (page 2491). It was crystallized from ethyl acetate and obtained in pale yellow crystals, which did not possess a sharp melting point, becoming molten when heated in a melting point tube to  $200^\circ$ . The following results were obtained on analysis:

Subst., I, 0.2568; II, 0.2392; cc. 0.1 *N*  $AgNO_3$ ; I, 14.20; II, 13.20.

Calc. for  $C_{24}H_{10}Cl_4O_{14}N_4$ : Cl, 19.70%. Found: I, 19.61; II, 19.57.

Tetranitrophenoltetrachlorophthalein diacetate is readily soluble in xylene and ethyl acetate. It is practically insoluble in methyl and ethyl alcohols, ether, acetone, and benzene. When boiled with dilute caustic alkali, it saponifies slowly, but only partially.

**Tetraaminophenoltetrachlorophthalein.**—Eight grams of tetranitrophenoltetrachlorophthalein were heated on a boiling water bath with 150 cc. of alcohol saturated with dry hydrochloric acid gas, and containing 80 g. of crystallized stannous chloride. The solution was diluted with a large amount of water and evaporated to about one-third of the original volume, in order to get rid of the alcohol. No separation of the amino compound or the tin chloride double salt took place, even on long standing. Hydrogen sulfide was then passed through the solu-

tion, diluted to 250 cc., until all the tin was removed. The filtered solution was evaporated to small bulk and carefully *neutralized* with ammonium hydroxide. The free base appeared as chocolate brown flocks, which were filtered off and dried. By crystallizing from ethyl alcohol, the tetraamino compound was obtained as a light brown, crystalline powder, which did not melt even when heated to 335°. The yield was very small, less than one gram of the purified product being obtained. The following results were obtained on analysis:

Subst., 0.2660; cc. 0.1 *N* AgNO<sub>3</sub>, 20.48.

Calc. for C<sub>24</sub>H<sub>14</sub>Cl<sub>4</sub>O<sub>4</sub>N<sub>4</sub>: Cl, 27.49%. Found: 27.30.

Tetraaminophenoltetrachlorophthalein differs markedly from the corresponding diamino compound in its greater solubility in the ordinary solvents. It dissolves readily in water while the diamino compound is almost insoluble. It dissolves in caustic alkalis and alkali carbonates with a blue color, which is not nearly as intense as that produced by the diamino compound. The alkaline solutions when exposed to the air are much more unstable than those of the diamino compound, the blue color soon changing to green and finally to a straw color.

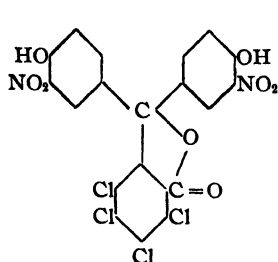
#### Theoretical.

By the action of nitric acid on phenoltetrachlorophthalein, a dinitro- and a tetranitro-derivative have been prepared. Although the positions of the nitro groups in these compounds have not been proven in this paper, it is logical to assume that the nitro groups enter each phenol molecule in the ortho positions to the hydroxyl groups and in the meta positions to the tetrachlorophthalic acid residue. Schestakoff and Nocken<sup>1</sup> state that both nitro groups in *dinitrophenolphthalein* are in the same phenol residue, but the evidence which they present to establish this view is by no means conclusive.<sup>2</sup> Although these nitro compounds of phenoltetrachlorophthalein are light yellow in color, it is probable that the color is due to the chromophoric action of the nitro groups and therefore the lactoid formula should be assigned to them. The ortho position of the nitro group in the phenol molecule probably conditions the color to some extent; for instance, orthonitrophenol has a marked yellow color, while paranitrophenol is colorless. From the above considerations the following formulas are assigned to the nitrophenoltetrachlorophthaleins (page 2499).

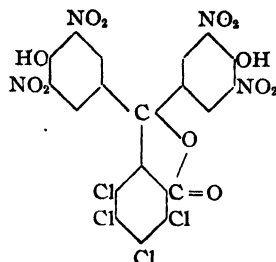
Dinitrophenoltetrachlorophthalein crystallizes from solvents in the anhydrous condition, while the tetranitro compound holds two molecules of water, which are not lost on remaining several days in a vacuum over phosphorus pentoxide. Since the latter compound dissolves readily in alkali bicarbonates, it can best be represented as a hydrate of the carbinol carboxylic acid.

<sup>1</sup> *Ber.*, 47, 331 (1914).

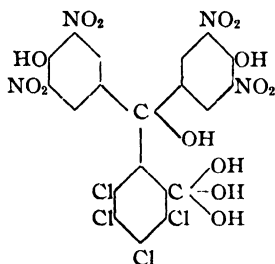
<sup>2</sup> Oddo, *Gazz. chim. ital.*, 43, II, 175 (1913) and *Ber.*, 47, 967 (1914).



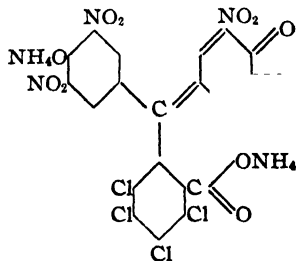
Dinitrophenol-tetrachlorophthalein.



Tetranitrophenol-tetrachlorophthalein.



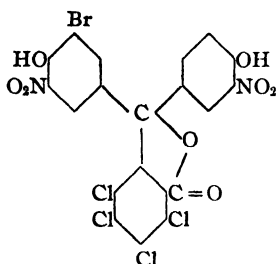
The fact that the tetranitro compound holds two molecules of water, while the dinitro derivative crystallizes in the anhydrous form, may be explained by the more marked acid properties of the former. This is clearly shown by the fact that tetranitrophenoltetrachlorophthalein dissolves in alkali bicarbonates while the dinitro derivative does not, and also by the fact that tetranitrophenoltetrachlorophthalein absorbs *five* molecules of ammonia while the dinitro compound absorbs but *four*. When these abnormal salts are exposed to the air the dinitro compound loses practically all of its ammonia while the tetranitro derivative forms a stable diammonium salt. This latter compound has a deep orange color and is best represented by the following quinoid formula:



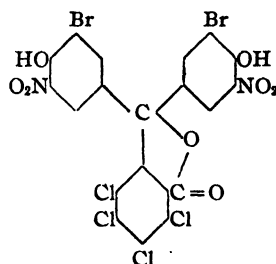
Diammonium salt of tetranitrophenoltetrachlorophthalein.

Monobromo- and dibromodinitrophenoltetrachlorophthaleins have been made by the bromination of dinitrophenoltetrachlorophthalein. These compounds have acid properties intermediate between those of the dinitro- and tetranitrophenoltetrachlorophthaleins. That both of

these bromo compounds have stronger acid properties than dinitrophenoltetrachlorophthalein is shown by the fact that they absorb more ammonia and that they have weaker acid properties than the tetranitrophenoltetrachlorophthalein by the fact that they do not decompose alkali bicarbonates. These compounds are therefore best represented by lactoid formulas.

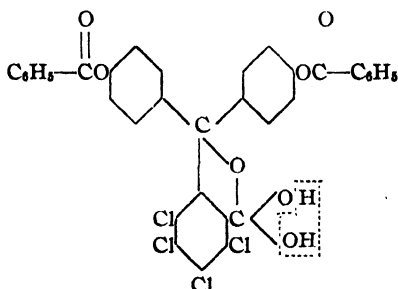


Monobromodinitro-  
phenoltetrachlorophthalein.

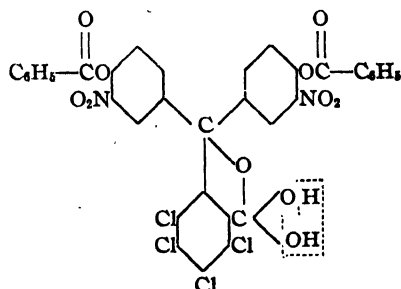


Dibromodinitro-  
phenoltetrachlorophthalein.

Phenoltetrachlorophthalein and dinitrophenoltetrachlorophthalein form colorless dibenzoates. Both crystallize from benzene with a molecule of water which is not lost on remaining several days in a vacuum over phosphorus pentoxide. In each case this form is probably the hydrate and not the carbinol acid since they are both insoluble in cold caustic alkalies.



Hydrate of  
phenoltetrachlorophthalein  
dibenzoate.

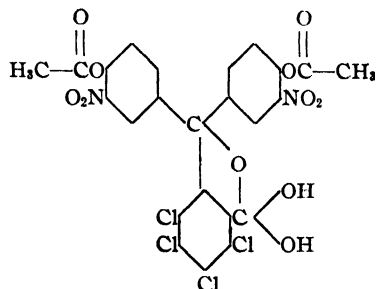


Hydrate of  
dinitrophenoltetrachloro-  
phthalein dibenzoate.

On heating to  $120^\circ$ , both compounds lose the molecule of water, as shown in the above formulas.

Dinitrophenoltetrachlorophthalein diacetate crystallizes from benzene in very pale yellow crystals, which hold two molecules of water, neither of which is lost on remaining several days in a vacuum over phosphorus pentoxide. On heating to  $105^\circ$  for an hour, one molecule of water is lost, and after continued heating at  $105^\circ$ , or more readily at  $140^\circ$ , the compound melts and the second molecule of water is lost. From acetone the compound crystallizes with only one molecule of water, which is lost

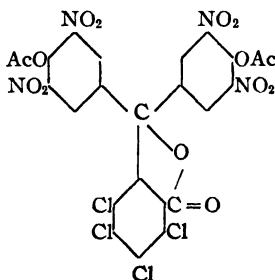
only at 140°. It seems highly probable, therefore, that the product from acetone is the hydrate



while the product from benzene is this hydrate with a molecule of water of crystallization. The fact that the substance is not soluble in the cold in caustic alkalis shows that it is not the carbinol carboxylic acid.

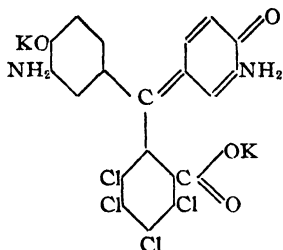
Oddo<sup>1</sup> made dinitrophenolphthalein diacetate, which he describes as a dimorphous body. It is very probable that the white product obtained by him from benzene is a hydrate, while the yellow form, obtained either by heating the white modification above its melting point, or by crystallizing it from alcohol, is the anhydrous diacetate.

Tetranitrophenoltetrachlorophthalein forms a colorless dibenzoate, and a very pale yellow diacetate. Since these compounds are insoluble in alkalis and possess little color, they probably have the lactoid structure and may be represented by the following formula in which Ac represents an acetyl or a benzoyl group:

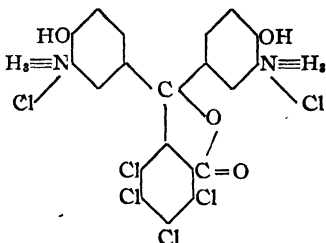


Diaminophenoltetrachlorophthalein is obtained by the reduction of dinitrophenoltetrachlorophthalein. It dissolves in alkalis with an intense Prussian blue color, while with hydrochloric acid it forms a colorless dihydrochloride, thus exhibiting the properties of both an acid and a base. That the basic properties are weak is shown by the fact that the hydrochloride is readily hydrolyzed by heating its aqueous solution. The structure of these compounds is best represented by the following formulas:

<sup>1</sup> *Gazz. chim. ital.*, 43, II, 175 (1913).

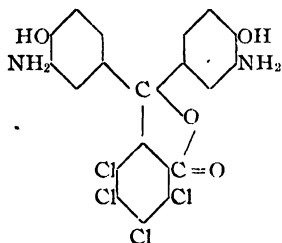


Dipotassium salt of  
diaminophenoltetrachloro-  
phthalein (colored).

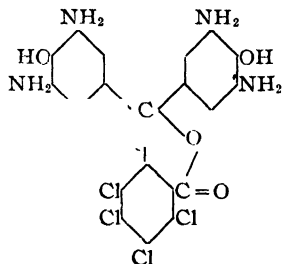


Dihydrochloride of  
diaminophenoltetrachloro-  
phthalein (colorless).

Tetraaminophenoltetrachlorophthalein results from the reduction of tetranitrophenoltetrachlorophthalein. Unlike the diaminophenoltetrachlorophthalein, it is readily soluble in hydrochloric acid solution. It dissolves in alkalis with only a faint blue color, which soon disappears on standing, probably owing to the formation of the salt of the carbinol acid. Diamino- and tetraaminophenoltetrachlorophthalein probably are best represented by the following structural formulas:



Diaminophenol-  
tetrachlorophthalein.



Tetraaminophenol-  
tetrachlorophthalein.

It is interesting to note that these phthaleins are *colored* (possibly due to an orthoquinoid condition) and that they form *colorless* salts with acids.

### Summary.

The results of this investigation may be briefly stated as follows:

1. Phenoltetrachlorophthalein has been made from tetrachlorophthalic acid and shown to be a chemical individual and not a mixture of isomers. In all probability both hydroxyl groups occupy the para positions to the methane carbon atom.
2. Dinitro- and tetranitrophenoltetrachlorophthalein have been prepared and the action of ammonia on these compounds has been studied.
3. The diacetates and the dibenzoates of the nitro compounds have been made, thus showing the presence of two hydroxyl groups.
4. The corresponding amino compounds have been obtained by the reduction of the nitro compounds. These compounds have both acid and

basic properties, dissolving in alkalis with a *blue* color and forming *colorless* hydrochlorides.

5. Monobromo- and dibromodinitrophenoltetrachlorophthalein have been prepared and the action of ammonia on these compounds has been studied.

6. The effect of introducing acid groups into the phenoltetrachlorophthalein molecule has been studied. Tetranitrophenoltetrachlorophthalein has the strongest acid properties; dinitrophenoltetrachlorophthalein the weakest, while the monobromo- and dibromodinitrophenoltetrachlorophthalein stand intermediate.

ITHACA, N. Y.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE SYRACUSE UNIVERSITY.]

## THE PYROGENETIC DECOMPOSITION OF AMIDES. I.

By R. S. BOEHNER AND C. E. ANDREWS.

Received September 11, 1916.

It is a well-known fact that, on distillation, the acid amides of both the aliphatic and aromatic series decompose to a very slight degree into the corresponding cyanides and water. Wöhler and Liebig<sup>1</sup> passed the vapor of benzamide through a red hot glass tube obtaining a small quantity of an oily liquid which was later identified as phenyl cyanide. In view of the decomposition of alcohols into ethylene hydrocarbons, or ethers, and water, on being passed through hot tubes filled with various materials,<sup>2</sup> it was thought possible that a more complete decomposition of the amides into cyanides and water might be effected by a similar method. Since the products of decomposition of amides, namely the cyanides and water, have a much lower boiling point than the amides, it was thought that the method referred to above might be modified by heating the amides with the contact material in a flask whose outlet was high enough to permit the cyanides and water to distill off, but would cause the amides to condense in the flask and drop back upon the hot contact material. The contact substances used were aluminium oxide, pumice stone, glass, sand, and graphite. By the above method and using the substances mentioned a much more complete decomposition of the amides into the cyanides and water was effected.

### Experimental.

A round-bottomed flask of 100 cc. capacity, containing the contact substance and amide, and provided with a ground-glass stopper with the outlet tube about 25 cm. above the bottom of the glass, was heated in an asbestos air bath. The heating was in each case regulated so that the

<sup>1</sup> *Ann.*, 3, 249 (1832).

<sup>2</sup> Ipatiew, *Ber.*, 34, 596, 3579 (1901); *Ibid.*, 35, 1047, 1057 (1902); *Ibid.*, 36, 1990 (1903); Sabatier and Mailhe, *Compt. rend.*, 146, 1376 (1908); *Ibid.*, 147, 106 (1908); *Ibid.*, 148, 1734 (1909).

cyanide and water formed would distil off but so that at the same time the amide would condense and return to the flask before the outlet was reached. The temperature, measured by a thermometer placed in the bath and outside the flask, naturally varied with the amide used and was probably not accurately observed. It was generally at  $250^{\circ}$  to  $260^{\circ}$ . The operation required about four hours for completion. The escaping water and cyanide vapors were condensed in an ordinary condenser and caught in a receiver cooled and closed as completely as possible in order to avoid loss by evaporation. The amount of cyanide obtained was determined according to the method of Gatterman,<sup>1</sup> a method which is not quantitative but gives low values.

The relative proportions in which to use the amides and contact substance were determined by repeated trials with acetamide and aluminium oxide. The best results were obtained using 50 g. of the oxide to 10 g. of the amide. In all the experiments thereafter 10 g. of any amide were employed and a volume of the finely ground contact substance equal to the volume of 50 g. of aluminium oxide.

In all the experiments the odor of ammonia was noticeable and there was a slight blackening of the contact material due to some slight carbonization.

In the case of formamide it was found that the amide distilled off practically unchanged. The procedure was therefore modified by heating the contact substance alone to  $250^{\circ}$  to  $300^{\circ}$  and then allowing the amide very slowly to drop upon the hot material in the flask. The hydrocyanic acid formed was passed into a solution of caustic potash and the amount of potassium cyanide formed was then determined by precipitation with standard silver nitrate solution and titration of the excess silver by Volhard's process.

Because of the high boiling point of phenylacetamide and its ready sublimation this method was found unsatisfactory, the greater part subliming over before decomposing into the cyanide and water.

Substance.	Aluminium oxide.		Pumice stone.		Glass.		Sand.		Graphite.	
	Wt. of cyanide.	% of theory.	Wt. of cyanide.	% of theory.	Wt. of cyanide.	% of theory.	Wt. of cyanide.	% of theory.	Wt. of cyanide.	% of theory.
Formamide	0.47	7.8	...	...	...	...	...	...	...	...
Acetamide	4.7	68.0	4.5	65.0	4.5	65.0	3.6	52.0	4.6	66.0
Propamide	4.2	56.0	4.6	61.0	5.5	73.0	...	...	4.7	62.0
Normal-butyramide	4.6	58.0	...	...	4.0	51.0	4.6	58.0	4.9	62.0
Iso-butyramide	5.3	67.0	...	...	4.9	62.0	...	...	5.7	72.0
Normal-valeramide	5.2	63.0	...	...	...	...	...	...	6.0	73.0
Iso-valeramide	4.7	57.0	...	...	6.1	74.0	...	...	5.8	71.0
Caproamide	6.1	72.0	...	...	...	...	...	...	6.1	72.0
Benzamide	4.6	54.0	4.7	55.0	5.5	64.0	...	...	5.8	68.0
Phenylacetamide	...	...	...	...	...	...	...	...	2.0	...

<sup>1</sup> "Practical Methods of Organic Chemistry," Third Edition, p. 155.



### Summary.

Acid amides may be decomposed very largely into the cyanides and water by heating in a flask with various substances—aluminium oxide, pumice stone, sand—the flask being provided with an outlet sufficiently far above the contact substance to permit the more volatile cyanide and water to escape while causing the amides to condense and drop back upon the hot contact material.

SYRACUSE, N. Y.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF SYRACUSE UNIVERSITY.]

## THE PYROGENETIC DECOMPOSITION OF AMIDES. II.

BY R. S. BOEHNER AND A. L. WARD.

Received September 11, 1916.

In the previous paper<sup>1</sup> it has been shown that the acid amides may be decomposed into the cyanides and water by heating with various contact materials but the method used did not permit of an accurate determination of the temperature at which the most complete decomposition could be effected. In order to determine this the amides were passed through hot tubes filled with these contact substances, the temperature being determined by a Hoskins' pyrometer. Using this method a temperature of about 425° was found to give the best results when passing acetamide through a tube filled with aluminium oxide and this temperature was employed in working with the other contact materials. It has thus been possible to effect practically a complete decomposition of the amides into cyanide and water, allowance being made for the lack of quantitative methods for the determination of the cyanides under the conditions obtaining in this work.

### Experimental.

Combustion tubing wrapped in asbestos paper was wound with "Nichrome" ribbon, this covered with several layers of asbestos paper, and the whole placed in an iron pipe which was also covered with asbestos paper. The current from a 110 volt lighting circuit served to give the required temperature. The pyrometer couple was enclosed in a hard glass tube before being placed in the combustion tubing. A. Mailhe,<sup>2</sup> endeavoring to reduce the amides by passing their vapors mixed with hydrogen over reduced nickel and copper, obtained unsatisfactory results because of the lack of volatility of the amides. In order to overcome this difficulty air was passed through the slightly boiling amide contained in a flask and thence passed by means of a glass tube into the furnace. In this way 20 g. of amide were completely and satisfactorily volatilized and carried over the contact material in the course of about five hours. In the case

<sup>1</sup> THIS JOURNAL, 38, 2503 (1916).

<sup>2</sup> Chem. Ztg., 31, 1146 (1907).

of-benzamide, however, it was found that the tube connecting the flask and furnace became clogged with the solid amide. Benzamide, contained in a porcelain boat, was therefore placed directly in the end of the inner tube of the furnace, and air passing over this when heated serving to carry it forward over the contact material. The pyrometer in this case measured the temperature between the two tubes of the furnace. The products of decomposition in all cases passed into a condenser and were collected and determined by the method mentioned in the previous paper.<sup>1</sup>

To determine what effect, if any, the air would have on the reaction below the point at which oxidation might take place, nitrogen was substituted for air and determinations were also made in which the amide vapors were made to pass over the contact material without the aid of gases. The amounts of methyl cyanide obtained from 20 g. of acetamide using aluminium oxide and pumice stone, respectively, as contact substances at a temperature of 425°, were as follows:

Aluminium oxide and with acetamide.

In presence of air gave	11.4 g. CH <sub>3</sub> CN.	82% of theory
In presence of nitrogen gave	9.3 g. CH <sub>3</sub> CN.	66.2% of theory
Without gases gave	7.2 g. CH <sub>3</sub> CN.	53.2% of theory

Pumice stone and acetamide.

	12.7 g. CH <sub>3</sub> CN.	91.5% of theory
	8.0 g. CH <sub>3</sub> CN.	57.5% of theory
	2.5 g. CH <sub>3</sub> CN.	18.0% of theory

Acetamide and propamide vapors along with air were passed through empty tubes, 10.8% and 10% of the theoretical yield being respectively obtained.

The general results are given in the following table, air being used in each case with 20 g. of amide at a temperature of about 425°:

TABLE I.

Substance.	Aluminium oxide.		Pumice stone.		Sand.		Graphite.	
	Wt. of cyanide.	% of theory.	Wt. of cyanide.	% of theory.	Wt. of cyanide.	% of theory.	Wt. of cyanide.	% of theory.
Acetamide.....	11.4	82.0	12.7	91.5	12.0	86.3	10.5	75.5
Propamide.....	13.0	86.1	13.5	89.4	13.5	89.4	..	..
Normal-butyramide.	13.2	83.0	14.0	88.0	14.0	88.0	..	..
Iso-butyramide.....	..	..	14.5	91.2	..	..	..	..
Iso-valeramide.....	..	..	14.7	89.1	..	..	..	..
Caproamide.....	13.9	80.9	15.0	89.3	..	..	..	..
Benzamide.....	..	..	..	..	13.6	90.6	..	..

The contact materials here used may be arranged in order of efficiency in promoting the decomposition of the amides as follows: Pumice stone, sand, aluminium oxide, and graphite. The variations in extent of decomposition with the different contact materials are but small and we are of the opinion that they may be explained by the differences in the state of division of the particles of the contact substances, the more finely divided providing a larger surface and being the more effective.

<sup>1</sup> THIS JOURNAL, 38, 2503 (1916).

A. Mailhe's<sup>1</sup> reduction of the amides to amines by passing the vapors of the former along with hydrogen over finely divided nickel and copper may be explained by assuming that the amides decompose into the cyanide and water and that the cyanides were then reduced to the amines. On passing acetamide over finely divided nickel at 180° to 200° without hydrogen it was found that a slight decomposition into cyanide and water had taken place.

### Summary.

The acid amides may be completely decomposed into the cyanides and water by passing their vapors along with air over various contact material at a temperature of about 425°.

SYRACUSE, N. Y.

[CONTRIBUTIONS FROM THE SHEFFIELD CHEMICAL LABORATORY OF YALE UNIVERSITY.]

## RESEARCHES ON AMINES. VI. THE UTILIZATION OF HYPOCHLORITE COLOR REACTIONS IN ESTABLISHING THE MECHANISM OF THE ACTION OF DIMETHYLSULFATE ON ANILINE.

By NORMAN A. SHEPARD.

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The method of alkylating amines recently proposed by Werner,<sup>2</sup> by means of which monomethylated amines can be obtained by alkylation with dimethylsulfate in benzene solution, gave promise of important practical applications. According to this investigator a primary amine like aniline and this ester interact in molecular proportions, under such conditions, giving practically a quantitative yield of the methylsulfuric acid salt of the monomethylated derivative. The transformation was expressed by him in the following manner:



Having occasion to apply this method for the production of methyl  $\beta$ -phenylethylamine,  $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{NHCH}_3$ , the writer was surprised to find that the crystalline addition product formed by interaction of dimethylsulfate and  $\beta$ -phenylethylamine did not give the desired alkyl derivative when decomposed with alkali. On the contrary, the greater portion of the original amine was recovered unaltered. In order to determine the cause of the failure to obtain alkylation in this case, attention was naturally turned to a study of Werner's reaction. This work has now been completed and the purpose of this paper is to record new data that have been obtained, which are not in accord with his interpretation.

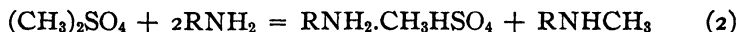
Previous to the work of Werner, Ullmann<sup>3</sup> had investigated the be-

<sup>1</sup> *Chem. Ztg.*, 31, 1146 (1907).

<sup>2</sup> *J. Chem. Soc.*, 105, 2762 (1914).

<sup>3</sup> *Ann.*, 327, 104 (1903).

havior of dimethylsulfate toward aniline. According to him, *two* molecular proportions of the base react with *one* of the ester in ether solution, forming one molecule of the methylsulfuric acid salt of aniline and leaving one molecule of monomethylaniline in solution as expressed in the following equation:



The writer has now obtained data which indicate clearly that the interpretation of Ullmann is the correct one. Using equimolecular proportions of aniline and ester and following the directions of Werner exactly, not only did the crystalline addition product prove to be the methylsulfuric acid salt of the *unalkylated* base, but the yields produced in no case approached the theoretical value based on his equation. In fact, these yields were only approximately one-half what should have been produced according to Equation 1. While 9.3 g. of aniline should yield theoretically 21.9 g. of addition product, in six separate experiments, taking special precautions to keep the temperature low and exclude moisture, the yields actually obtained were 13.7, 9.9, 11.2, 10.25, 12.5 and 11.1 g., respectively. On the other hand, these yields approach very closely the calculated value according to Ullmann's interpretation, 10.25 g., in fact, being exactly the theoretical quantity based on Equation 2. That the addition product was the methylsulfuric acid salt of aniline and not methylaniline, was shown by decomposing it with strong alkali. The base, which separated as an oil, was identified as unaltered aniline by its color reaction with hypochlorite solution, by conversion into its hydrochloride, and further by transformation into *sym.* diphenylthiourea when treated with phenylisothiocyanate. Thus the yields and chemical nature of the crystalline addition product confirm the conclusions of Ullmann.

The course of the reaction, however, varied somewhat from that described by Ullmann. It will be seen, when using equimolecular proportions of ester and base, that, after the first stage of the reaction is complete, one-half of the dimethylsulfate should still remain unaltered. This complicates the reaction considerably, for the monomethylaniline does not remain free in the benzene solution under such conditions, but separates in the form of an oil as the salt of methylsulfuric acid as expressed in Equation 3, and the tertiary base simultaneously formed, can then also

$$2\text{CH}_3\text{NHC}_6\text{H}_5 + (\text{CH}_3)_2\text{SO}_4 = \text{C}_6\text{H}_5\text{NHCH}_3.\text{CH}_3\text{SO}_4\text{H} + \text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2 \quad (3)$$

further react with the excess of ester, giving a methylsulfuric acid salt, as has been shown by Claesson and Lundvall.<sup>1</sup> These various stages in the reaction can actually be demonstrated by keeping the temperature of the reaction mixture at 0°. The progress of the alkylation can then be readily observed and followed by means of the hypochlorite

<sup>1</sup> *Ber.*, 13, 1703 (1880).

color reactions. If the oily addition product, formed in the second stage of the reaction, begins to separate before the crystalline product is removed, it clings very tenaciously to the latter and it is for this reason that the yields of the latter recorded above lack greater uniformity. This oil was never entirely homogenous. It consisted chiefly of the methylsulfuric acid salt of methylaniline but always contained some aniline and dimethylaniline also in combination as methylsulfuric acid salts. The product of the reaction was thus *not* exclusively a salt of monomethylaniline as claimed by Werner, but a mixture consisting of the salts chiefly of unaltered material with some mono- and di-alkylated base, but with these latter forms not in sufficient quantity to make the application of equimolecular proportions of base and ester in cold benzene solution of any practical value for alkylating purposes.

Further proof for Ullmann's interpretation of this reaction is found in the fact that the yield of crystalline addition product is largely increased on using two molecular proportions of aniline. Werner states, to the contrary, that under these conditions the excess of aniline was recovered unaltered in the mother liquors. The writer finds that the yield is largely increased with these proportions, giving 88% of the theoretical quantity of crystalline addition product based on Equation 2.

Werner based his entire proof, that the crystalline product was a derivative of methylaniline, on a hypochlorite color reaction for this base. In view of the fact that Beilstein's *Handbuch*<sup>1</sup> states that this base gives no coloration with bleaching powder solution, as is also stated of both methyl- and dimethylaniline in the latest edition of Richter's *Organische Chemie* (1913), it seemed of distinct value to make a comparative study of all the hypochlorite color reactions of these three bases. It was found that, under certain conditions, each of these bases gives a well-defined and characteristic color reaction with bleaching powder solution and the results of this work are recorded in Tables I and II, illustrating the behavior in different concentrations. The deep reddish purple coloration produced by aniline in neutral or alkaline solution with bleaching powder solution, discovered by Runge,<sup>2</sup> confirmed by Hofmann,<sup>3</sup> and carefully studied by Nietzki,<sup>4</sup> is a very satisfactory color test for this base. The writer has found, however, that in the presence of large amounts of methylaniline (25% or more), the test is unreliable, giving only an indefinite brown precipitate with no purple coloration. The first observation, as far as the writer is aware, of a hypochlorite color reaction for methyl- and dimethylaniline, is recorded by Willm and Girard.<sup>5</sup> These investigators

<sup>1</sup> Vol. II, p. 325.

<sup>2</sup> *Pogg. Ann.*, 31, 66 (1834).

<sup>3</sup> *Ann.*, 47, 54 (1843).

<sup>4</sup> *Ber.*, 27, 3263 (1894).

<sup>5</sup> *Bull. soc. chim.*, 28, 49 (1877).

state that the former gives a dark blue-violet and the latter a yellow color with bleaching powder solution, but no mention of the conditions, such as concentration or acidity, under which these colors were obtained, was made. Three years previous to this, Hofmann<sup>1</sup> made the observation that methylaniline gives no coloration with hypochlorite solution, which is absolutely correct, *provided the solution is neutral*. In *alkaline* solution Leech<sup>2</sup> has recently shown that this base gives a fine transient navy blue, easily distinguishable from the aniline coloration. The writer has found this test to be very satisfactory indeed and more sensitive to traces of methylaniline than the method of testing in *acid* solution employed by Werner (cf. Table II). This latter method consists in adding bleaching powder solution and then a few drops of dilute sulfuric acid to an aqueous solution of the base, when a deep indigo-blue color develops if methylaniline is present. This test is very brilliant and quite satisfactory, provided the reagents are added in the order given above, *i. e.*, bleaching powder solution *first* and *then* the acid. It has now been found on the other hand that if the order of adding the reagents is reversed and the bleaching powder solution is added to an acid solution of the base, aniline also will give a deep navy blue color, very easily confused with that produced by methylaniline. In fact only on very careful observation can the two colors be distinguished, but when compared side by side it was found that the blue produced by aniline is less brilliant, almost always murky and distinctly more fugitive than that produced by methylaniline. On short standing (about one hour), it changes to a murky brown suspension, while the test with methylaniline will remain clear and retain its intensity without appreciable fading for twenty-four hours. Even after forty-eight hours the color is still quite brilliant. It is advisable in this test to use a moderate excess of bleaching powder solution, but an excess of sulfuric acid should be avoided.

It can now readily be seen how Werner drew wrong conclusions from his color test. A water solution of the crystalline addition product,  $C_6H_5NH_2 \cdot CH_3SO_4H$ , is strongly acid to litmus paper and therefore on adding bleaching powder solution all conditions are favorable for producing the navy blue color from aniline. The writer has found that the water solution of his addition product gives an excellent deep navy blue when tested as Werner directed. If, however, the methylsulfuric acid is first neutralized before testing, this navy blue color is not obtained and the familiar reddish purple of aniline appears. As Werner made no attempt apparently to liberate the free base and identify it other than through this color reaction, he failed to realize that this navy blue was not peculiar

<sup>1</sup> *Ber.*, 7, 526 (1874).

<sup>2</sup> *THIS JOURNAL*, 35, 1042 (1913).

to methylaniline alone and therefore gave an erroneous interpretation to his reaction.

To identify dimethylaniline, Werner employed the deep orange-yellow color reaction, first mentioned by Willm and Girard,<sup>1</sup> but he does not state the conditions necessary for the successful production of this coloration. The writer finds that this test is very satisfactory and reliable, provided it is carried out in a slightly *acid* medium, for this base gives no coloration in neutral or alkaline solution. Strong acid solutions, however, should be avoided, for the test may be entirely negative under such conditions; the yellow color is quickly destroyed by alkalies or a large excess of calcium hypochlorite solution.

TABLE I.—COMPARATIVE COLOR TESTS FOR ANILINE, METHYL- AND DIMETHYLANILINE.

Concentration of base: 1 drop of base in 5 cc. H<sub>2</sub>O for each test.

Concentration of CaOCl<sub>2</sub> solution: one-half saturated.

Base.	Reagents		
	0.5 cc. CaOCl <sub>2</sub> .	0.5 cc. CaOCl <sub>2</sub> followed by 3 drops dil. H <sub>2</sub> SO <sub>4</sub> .	3 drops dil. H <sub>2</sub> SO <sub>4</sub> followed by 0.5 cc. CaOCl <sub>2</sub> .
C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	Deep reddish purple <i>characteristic</i> Changed to brown by excess CaOCl <sub>2</sub>	Dark murky bluish green	Deep reddish purple, changing to deep indigo-blue
C <sub>6</sub> H <sub>5</sub> NHCH <sub>3</sub>	Yellowish to brownish murky solution	Very intense indigo-blue ( <i>x</i> ) <i>characteristic</i>	Indigo-blue developing more slowly than <i>x</i>
C <sub>6</sub> H <sub>5</sub> N(CH <sub>3</sub> ) <sub>2</sub>	Colorless murky solution	Deep orange-yellow <i>characteristic</i>	Deep orange-yellow <i>characteristic</i>

TABLE II.—COMPARATIVE COLOR TESTS FOR ANILINE, METHYL- AND DIMETHYLANILINE.

Concentration of base: 1.0 cc. <sup>1</sup>/<sub>100</sub> mole solution of base for each test.

Concentration of CaOCl<sub>2</sub>: one-half saturated.

Base.	Reagents.		
	1 drop CaOCl <sub>2</sub> .	1 drop CaOCl <sub>2</sub> followed by 1 drop dil. H <sub>2</sub> SO <sub>4</sub> .	3 drops 6 N NaOH followed by 0.5 cc. CaOCl <sub>2</sub> .
C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	Deep reddish purple <i>characteristic</i>	Insignificant pink or brown	White precipitate and deep purple solution
C <sub>6</sub> H <sub>5</sub> NHCH <sub>3</sub>	Insignificant yellow with slight turbidity	Insignificant pale blue	White precipitate with distinct navy blue color developing slowly and then slowly fading to yellow <i>characteristic</i>
C <sub>6</sub> H <sub>5</sub> N(CH <sub>3</sub> ) <sub>2</sub>	Colorless	Deep orange <i>characteristic</i>	White precipitate

### Experimental Part.

The Action of Dimethylsulfate on Aniline at Room Temperature.—To 9.3 g. of aniline (freshly distilled) in 75 cc. of benzene (distilled over

<sup>1</sup> *Loc. cit.*

sodium), 12.6 g. of dimethylsulfate (1 mol) in 25 cc. of benzene were added cooling at first to prevent any rise in temperature. Every precaution was taken to have all the reagents absolutely dry and the ester was washed with sodium bicarbonate to remove any methylhydrogen sulfate, carefully dried and then twice distilled *in vacuo* before use. The crystalline addition product began to separate almost immediately and, after standing for 24 hours at room temperature, was filtered by suction. A thick, yellow oil adhered to the crystals, which was partially removed by thorough pressing out and washing with benzene. After drying over concentrated sulfuric acid, the last traces of this oily material were pressed out on a porous plate. The weight was then 9.9 g. The yield of this crystalline addition product will vary considerably; in three duplicate experiments 9.3 g. of aniline yielded 13.7, 11.2, and 10.25 g., respectively. In every case, even after long drying, the products were oily and did not melt sharply. The water solution was acid but did not give a precipitate with barium chloride. When this addition product was decomposed in aqueous solution with strong potassium hydroxide, a yellowish brown oil separated, which was extracted with ether and dried over caustic potash. Dry hydrochloric acid was then passed into this ether solution, when aniline hydrochloride separated as crystals melting at  $198^{\circ}$ .

The benzene mother liquor from the crystalline product contained a yellow oil, insoluble in benzene, which became dark green on standing. The benzene was decanted from this oil and allowed to stand, when more oil gradually deposited. An aqueous solution of this oil was acid to litmus, gave no test for sulfates with barium chloride, but gave a strong color reaction for methylaniline. When decomposed with sodium hydroxide, 1.4 g. of mixed bases were liberated. Treatment of this mixture with phenylisothiocyanate gave 0.5 g. of *sym.* diphenylthiourea (corresponding to 0.2 g. of aniline) and 0.7 g. of methyldiphenylthiourea (corresponding to 0.3 g. of methylaniline). These urea derivatives were separated by crystallization from alcohol, when the former separated in plates, melting at  $150-1^{\circ}$ . The alcohol mother liquor did not deposit crystals and it was only after removing the alcohol, triturating with petroleum ether and cooling to  $-16^{\circ}$ , that the methyldiphenylthiourea would deposit in a crystalline state. This was then recrystallized from alcohol when it separated in stout prisms, melting at  $85-7^{\circ}$ . No lowering of the melting point was observed, when both these urea derivatives were mixed with the corresponding pure substance. Extraction of the residues from the mother liquors of the thiourea derivatives, with dilute hydrochloric acid and neutralization of the resulting solution with potassium hydroxide, gave 0.6 g. of a light brown oil. The solution of this oil in 3.0 g. of 20% hydrochloric acid, cooled to  $-5^{\circ}$  and then treated with 0.35 g. of sodium nitrite dissolved in the least possible quantity of water, deposited 0.5 g.



of a deep orange-yellow powder, which decomposed with explosive violence at  $165-7^{\circ}$ . Though decomposing somewhat low, it agreed in all its properties with *p*-nitroso-dimethylaniline hydrochloride (m. p.  $177^{\circ}$ ), which was prepared for comparison.

The original benzene solution was now allowed to evaporate spontaneously. About 2.0 g. of oil remained, which was soluble in water. Bleaching powder solution showed this to be a mixture of dimethylaniline with some methylaniline, both in the form of salts. An aqueous solution is acid, but gives no precipitate with barium chloride.

**The Action of Dimethylsulfate on Aniline at  $0^{\circ}$ .**—The above reaction was repeated, using the same proportions, but allowing the reaction to proceed at continued low temperature in a refrigerator. After standing for 15 hours, the crystalline addition product was pure white but, at the end of 18 hours, a very light yellow color was beginning to appear. Upon filtering at once, 12.5 g. of addition product (after drying over sulfuric acid) were obtained. It was only very slightly oily and no oil had as yet separated in the benzene mother liquor. In a duplicate experiment, also carried out at  $0^{\circ}$ , the salt was filtered after 3.5 hours. The deposition of addition product was not yet complete, under these conditions, but there was no oil and the product was pure white. On standing 16 hours longer, still at  $0^{\circ}$ , the remainder of the product, separating in crystalline leaves and free from any oil, deposited, bringing the total yield up to 11.1 g. It melted sharply at  $158-60^{\circ}$ , gave no test for sulfate and on prolonged exposure to the air did not appear particularly hygroscopic. The aqueous solution was strongly acid and gave a strong color reaction for aniline with calcium hypochlorite after neutralization with alkali. Liberation of the free base with alkali and treatment with phenylisothiocyanate gave *sym.* diphenylthiourea in 66% yield (after complete purification).

Calc. for  $C_7H_{11}O_4NS(C_6H_5NH_2 \cdot CH_3SO_3H)$ : N, 6.83. Found: N, 6.67, 6.68.

Titration with 0.1061 *N* KOH, using phenolphthalein as the indicator:

I. 0.1803 g. required 8.35 cc. II. 0.4039 g. required 18.75 cc. KOH.

Calc. for  $C_7H_{11}O_4NS$ :  $CH_3SO_3H$ , 54.63. Found:  $CH_3SO_3H$ , 55.06, 55.19.

The benzene mother liquor, containing *no* oil, was allowed to stand at  $0^{\circ}$ . The yellow oil soon began to separate. The benzene was decanted after 29 hours' standing at  $0^{\circ}$  and then let stand at room temperature for 2 days. A second crop of oil had then separated. The benzene solution, which, previous to the second deposition of oil, had given color tests for both mono- and di-methylaniline, now gave *no* test for the former, but a strong test for the latter. The combined oily layers weighed about 6.0 g., but contained a considerable quantity of benzene. This yellow oil turned green on standing as before and an aqueous solution was acid to litmus but gave no test for sulfuric acid. It gave a strong test for

methylaniline, but was not homogeneous, for, on conversion into thio-urea with phenylisothiocyanate as in the previous experiment, 1.6 g. of free bases gave about 0.3 g. of *sym.*-diphenylthiourea (corresponding to 0.12 g. of aniline), 1.5 g. of methyl-diphenylthiourea (corresponding to 0.7 g. of methylaniline), and 0.2 g. of dimethylaniline was extracted from the residues by hydrochloric acid. The last product was identified by the deep yellow coloration produced by bleaching powder in acid solution.

The benzene mother liquor from the yellow oil left a residue of 2.7 g. on spontaneous evaporation, which consisted of a light yellow syrup containing a few drops of a non-miscible brownish oil, which did not dissolve when treated with water. This was extracted with ether (weight = 0.10 g.); it was not dimethylaniline as shown by color tests, but, on boiling with caustic soda, the white precipitate with barium chloride in acid solution indicated that it was unaltered dimethylsulfate. The water soluble portion of the above residue gave no precipitate with barium chloride until saponified with boiling alkali; the test for sulfate was then strong. Sodium hydroxide liberated 0.15 g. of oil which was identified, by its color reactions and also by conversion into *p*-nitrosodimethylaniline hydrochloride, as dimethylaniline.

**The Action of One Molecular Proportion of Dimethylsulfate on Two Molecular Proportions of Aniline at 0°.**—Three and five-tenths grams of dimethylsulfate in 7 cc. of benzene were added to 5.2 g. of aniline (2 molecular proportions), in 21 cc. of benzene and the mixture allowed to stand for 16 hours in a refrigerator. The product, which was not oily, weighed 5.0 g. after standing for one week over concentrated sulfuric acid. This yield corresponds to 88% of the theoretical quantity, calculated from Ullmann's equation. The benzene mother liquor was a light brown color and contained no oil. This was allowed to stand for 8 hours at 0°; no oil deposited. A water extract of a portion of the now deep brown benzene solution gave a strong color test for methylaniline. After standing for several days at room temperature, only a trace of oil separated.

NEW HAVEN, CONN.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

## ACTION OF OXALYL CHLORIDE ON PRIMARY, SECONDARY AND TERTIARY ALCOHOLS.

BY ROGER ADAMS AND L. F. WEEKS.

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Staudinger,<sup>1</sup> who was the first to find a convenient method for the preparation of pure oxalyl chloride, studied several of its reactions. He found that it reacted normally with ethyl alcohol to give ethyl oxalate,

<sup>1</sup> *Ber.*, 41, 3558 (1908); 46, 1426 (1913); *Chem. Zentr.*, 1910, I, 307.

with ammonia and amines to give oxamides. He used it in certain Friedel and Craft's<sup>1</sup> syntheses in the hope of preparing 1,2-diketones, but obtained such compounds in only a few cases. In general, the reaction products were the same as he would have obtained if he had used phosgene. Thus, oxalyl chloride had broken down to phosgene and carbon monoxide before reacting. Staudinger<sup>2</sup> studied the action of oxalyl chloride in Friedel and Craft's reactions more carefully a few years later, and found that the speed of the reaction had much to do with the products which resulted; if a fairly active hydrogen was present in the benzene molecule, as the para hydrogen in anisol, then the reaction took place quickly, and anisil was produced; if unsubstituted benzene were used where there is no active hydrogen, then the oxalyl chloride decomposed first and benzophenone was produced. Liebermann<sup>3</sup> studied the action of oxalyl chloride with and without anhydrous aluminum chloride, on anthracene, ditolyl, indene, etc., and obtained similar results. If he used high temperatures and no aluminum chloride, products the same as those which would form from phosgene were produced, at low temperatures and in the presence of aluminum chloride diketones. In every case, however, the yields of the diketones were small.

The action of oxalyl chloride on mercaptans<sup>4</sup> gave thioesters and on aminoacids,<sup>5</sup> hydrazines,<sup>6</sup> ureas,<sup>7</sup> the normal oxalic acid derivatives in practically all cases, a few exceptions<sup>8</sup> being noted when oxalyl chloride acted like phosgene.

One other interesting and general reaction of oxalyl chloride was discovered by Staudinger<sup>9</sup> who noted the similarity of oxalyl chloride to certain inorganic acid chlorides. Various aldehydes and ketones reacted very readily with it, and gave good yields of products the same as those obtained with phosphorus pentachloride.

Sometime ago it was found in this laboratory,<sup>10</sup> that oxalyl chloride and pyridine reacted at low temperatures with phenols to give quantitative yields of the phenyl or substituted phenyl esters. It was observed, however, during this work, that if the reactions between certain of the phenols and oxalyl chloride were carried out at room or at higher temperatures,

<sup>1</sup> *Ber.*, 41, 3558 (1908); 42, 3485 (1909).

<sup>2</sup> *Ibid.*, 45, 1594 (1912).

<sup>3</sup> *Ibid.*, 44, 203, 852, 1453 (1911); 45, 1186 (1912); 46, 198 (1913).

<sup>4</sup> *J. Chem. Soc.*, 95, 1904, 1909 (1909).

<sup>5</sup> *Chem. Zentr.*, 1911, I, 1548; 1912, II, 910; 1913, II, 1739; *THIS JOURNAL*, 32, 121 (1910).

<sup>6</sup> *Rec. trav. chim.*, 34, 34 (1914).

<sup>7</sup> *Ber.*, 36, 1404 (1913).

<sup>8</sup> *Chem. Zentr.*, 1910, II, 931, 1422.

<sup>9</sup> *Ber.*, 42, 3966 (1909).

<sup>10</sup> *THIS JOURNAL*, 37, 2716 (1915).

dehydration products and not simple esters resulted. It seemed possible, therefore, that if oxalyl chloride were made to react with alcohols under the right conditions, it might act as a dehydrator and ethylene derivatives would result. Oxalyl chloride would be an especially good reagent for such a purpose, since all of the products of the reaction, except the unsaturated compound, would be gaseous. To test this we have taken different types of primary, secondary and tertiary alcohols and tried the action of oxalyl chloride on them. Different alcohols yielded different products, and although we have not yet studied a sufficient number so that a complete generalization may be made as to the exact reaction which will take place, we give below the results already in hand.

As characteristic primary alcohols, we chose *n*-propyl, isobutyl, isoamyl and benzyl alcohols, and allowed oxalyl chloride to act directly on them at room temperatures in the proportion of two molecules of alcohol to one of acid chloride. In each case, immediate reaction took place, and simple esters formed, just as Staudinger found with ethyl alcohol. The esters resulting were very pure and the yields were practically quantitative. For a rapid and convenient method of obtaining small amounts of pure oxalic acid esters of primary alcohols, the above is certainly to be recommended. We tried glycol also, and used the proportion one molecule of diatomic alcohol to one molecule of oxalyl chloride; the cyclic ester, ethylene oxalate, resulted.

For secondary alcohols, we studied benzhydrol, phenyl methyl carbinol and menthol. Benzhydrol in benzene solution gave a small yield of a white solid which proved to be benzhydryl ether. Phenyl methyl carbinol and menthol we treated without a solvent, and obtained in both cases as principal products the corresponding unsaturated compounds styrene and menthene. Small amounts of impure higher boiling products which formed in these last two reactions, we have not worked up, but the boiling points indicated that they were not the corresponding chlorides or oxalates. It was very possible, therefore, that in these instances some carbonates had formed. In general, the purity and yields of the products from the secondary alcohols were not very satisfactory. Possibly a change in conditions, however, might improve them.

For tertiary alcohols, we chose trimethyl carbinol, dimethylethyl carbinol, triphenyl carbinol and pinakone, and treated in each case (except with pinakone) two molecules of alcohol with one of chloride; with pinakone we used one molecule of alcohol to one of chloride. The triphenyl carbinol was dissolved in benzene, but no solvent was used with the others. Instantaneous reaction took place, and the first three yielded chlorides, oxalic acid separating out at the same time. Although the yields and the purity of the chlorides were not so extremely good as the yields and purity of the esters formed by the action of primary alcohols,

still they were very satisfactory. Pinakone reacted differently, as might be expected, since there is a great tendency here for water to split out and for a subsequent rearrangement into pinakoline. We were able to isolate two products, pinakoline and a solid which proved to be the corresponding carbonic acid ester. Here oxalyl chloride reacted like phosgene, and each chlorine atom then combined with a hydrogen atom of a hydroxyl group, yielding a cyclic carbonate.

In conclusion, our work has shown that oxalyl chloride reacts in several ways with alcohols. Primary alcohols go very smoothly to esters, most tertiary alcohols give good yields of chlorides, secondary alcohols and certain tertiary alcohols yield different types of products, dehydration products, such as ethers, or more generally, where such a reaction is possible, unsaturated compounds with small amounts of carbonic acid derivatives as secondary products.

We are now studying the action of oxalyl chloride and pyridine at low temperatures on different kinds of alcohols, and have already obtained oxalates with certain secondary alcohols. We hope this will be general with all alcohols, in which case, on account of the ease of formation at such a low temperature, the quantitative yields produced, and the ease with which the compounds produced, crystallize, we will show oxalyl chloride to be a convenient and valuable reagent for hydroxyl groups.

#### EXPERIMENTAL PART.

##### Primary Alcohols.

1. *N*-Propyl Alcohol, Isoamyl Alcohol, Isobutyl Alcohol.—In these experiments, a small boiling flask with the side arm attached to a condenser was used. The neck of the flask was fitted with a cork stopper holding a separatory funnel. The pure alcohols (2 mols), *n*-propyl, isobutyl or isoamyl, were placed in the flask and oxalyl chloride (1 mol) was allowed to drop very slowly from the funnel into the alcohol. The contents of the flask immediately heated up and fumes of hydrochloric acid gas were given off. When all the oxalyl chloride had been added, the contents of the flask were simply distilled. The weight of the crude distillate in each case corresponded to practically a quantitative yield of ester. On careful redistillation very pure esters resulted.

*n*-Propyl oxalate,  $(C_3H_7)_2C_2O_4$ , b. p. 211–212°.

Isobutyl oxalate,  $(C_4H_9)_2C_2O_4$ , b. p. 228–229°.

Isoamyl oxalate,  $(C_5H_{11})_2C_2O_4$ , b. p. 267–268°.

2. Benzyl Alcohol.—Benzyl alcohol (2 mols) was heated with oxalyl chloride (1 mol) in the same manner as the above alcohols. After the addition of the chloride, however, the reaction product was allowed to cool and a white crystalline mass formed in the flask. This was crystallized from alcohol, thus yielding practically a quantitative yield of pure benzyl oxalate.

Benzyl oxalate,<sup>1</sup>  $(C_6H_5CH_2)_2C_2O_4$ , m. p. 80.5–81.5°

3. **Glycol.**—Oxalyl chloride (1 mol) and glycol (1 mol) were allowed to react and then cooled as in the case of the benzyl oxalate. A pasty mass formed which, crystallized from ethyl oxalate, gave a m. p. 153°, and was undoubtedly the same compound as that which Bischoff<sup>2</sup> obtained from ethyl oxalate and glycol.

Ethylene oxalate,  $C_2H_4C_2O_4$ , m. p. 153°.

### Secondary Alcohols.

1. **Benzhydrol.**—A small flask with the benzhydrol (2 mols) dissolved in warm benzene was fitted with a stopper holding a reflux condenser and a small dropping funnel containing the oxalyl chloride (1 mol). The oxalyl chloride was allowed to run in slowly and the mixture then refluxed for half an hour. On spontaneous evaporation, an oil resulted which, on standing, gradually solidified to a pasty crystalline mass. This was clay-plated, then crystallized from alcohol, and was proved by analysis to be benzhydrol ether. The yield was about 30% of the theory. M. p. 107.5–108°.

Calc. for  $[(C_6H_5)_2CH]_2O$ : C, 89.14%; H, 6.28%. Found: C, 88.72; H, 6.45.

2. **Phenyl Methyl Carbinol.**—Phenyl methyl carbinol (2 mols) in an apparatus similar to that used for the primary alcohols was treated with oxalyl chloride (1 mol). The reaction mixture was distilled under diminished pressure (about 40 mm.) and yielded a main fraction boiling under 100° and a small fraction boiling at a much higher temperature. Oxalic acid remained behind in the distilling flask. The chief product was treated with bromine until no more was readily absorbed at a low temperature. A white crystalline mass resulted which after one recrystallization proved to be pure styrene bromide, thus showing styrene to be the main compound formed in the reaction. The small portion of higher boiling material was not studied further.

3. **Menthol.**—The reaction was carried out in the same way as for phenyl methyl carbinol, except that here a simple instead of a vacuum distillation was undertaken. Most of the distillate came over below 215° and rapidly absorbed bromine to form menthene bromide, thus proving menthene to be the chief product of the reaction. The material boiling above 215°, as it was so small in amount and so impure, was not studied further, but since it was higher boiling than menthyl chloride and lower boiling than menthyl oxalate, we concluded it was probably impure menthyl carbonate.

### Tertiary Alcohols.

1. **Trimethyl Carbinol, Dimethylethyl Carbinol.**—The same apparatus was used as for the primary alcohols. During the addition of the oxalyl

<sup>1</sup> *Ber.*, 35, 3441 (1902).

<sup>2</sup> *Ibid.*, 40, 2806 (1907).

chloride, oxalic acid gradually separated out of the reaction mixture. On distillation trimethyl chloromethane, in one case, and dimethyl ethyl chloromethane in the other, were produced in good yields. On redistillation, the chlorides were readily purified.

Trimethyl chloromethane,  $(\text{CH}_3)_3\text{CCl}$ , b. p.  $51-52^\circ$ . Dimethyl ethyl chloromethane,  $(\text{CH}_3)_2\text{C}_2\text{H}_5\text{CCl}$ , b. p.  $84-86^\circ$ .

2. **Triphenyl Carbinol.**—Triphenyl carbinol (2 mols) was dissolved in benzene in an ordinary flask, the stopper of which was fitted with a reflux condenser and a dropping funnel holding the oxalyl chloride (1 mol). On addition of the chloride, instantaneous reaction took place. After warming gently a short time, the mixture was allowed to evaporate and the resulting solid crystallized from benzene. It proved to be triphenyl chloromethane.

Triphenylchloromethane,  $(\text{C}_6\text{H}_5)_3\text{CCl}$ , m. p.  $100-101^\circ$ .

3. **Pinakone.**—Pinakone (1 mol) was treated directly with oxalyl chloride (1 mol) in an apparatus similar to that used with the primary alcohols. On distillation of the reaction mixture, a liquid boiling between  $100-128^\circ$  resulted, which proved to be impure pinakolin. A reddish residue left in the flask solidified on cooling and crystallized from alcohol in long, white needles, which on analysis were found to be the carbonate of pinakone. M. p.  $176-177^\circ$ .

Calc. for  $[(\text{CH}_3)_2\text{C}]_2\text{CO}_3$ : C, 58.33%; H, 8.33%. Found: C, 58.34; H, 8.28.  
CAMBRIDGE, MASS.

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[CONTRIBUTION FROM THE UNIVERSITY CHEMICAL LABORATORY OF OXFORD.]

## THE CRYSTALLIZATION OF CALCIUM TARTRATE.

By F. D. CHATTAWAY.

Received September 13, 1916.

Few salts have been more frequently prepared than calcium tartrate on account of its employment for the recognition of the acid and it is therefore surprising to find that little is known of its behavior when crystallizing from aqueous solution. When a soluble calcium salt is added to a neutral solution of a soluble tartrate the compound which first separates is not the ordinary orthorhombic tetrahydrated salt,  $\text{C}_4\text{H}_4\text{O}_6\text{Ca} \cdot 4\text{H}_2\text{O}$ , but a hexahydrated form,  $\text{C}_4\text{H}_4\text{O}_6\text{Ca} \cdot 6\text{H}_2\text{O}$ , which crystallizes in long, slender needles. This is unstable at the ordinary temperature and transforms with loss of two molecules of water into the well known tetrahydrated salt, small crystals of which quickly make their appearance among the needle-shaped crystals and grow at the expense of the latter, which dissolve and ultimately disappear.

### Experimental Part.

When equal volumes of 0.2 *N* solutions of calcium chloride and potassium sodium tartrate are mixed the liquid remains clear for a short time,

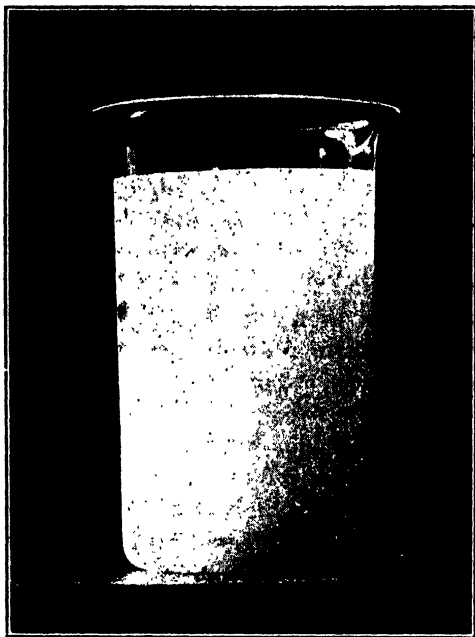


Fig. 1.

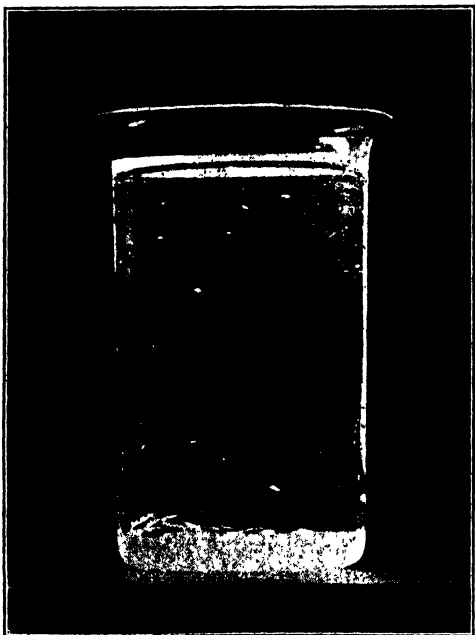


Fig. 2

then small tufts of needle-shaped crystals make their appearance and rapidly grow until in a few minutes the whole is filled with such tufts which finally interlace, a felted mass of crystals resulting which can be inverted without any of the mother liquor escaping. If kept at the ordinary temperature small crystals of the orthorhombic tetrahydrated form of calcium tartrate soon make their appearance and grow rapidly while the unstable needle-shaped crystals dissolve and finally disappear. The orthorhombic crystals thus produced, which are very finely shaped and often of considerable size, sink down in the beaker and form a comparatively thin layer. If the crystalline pulp of needle-shaped crystals be stirred or shaken vigorously, transformation is more rapid and after a few minutes the needle-shaped form is converted into the compact form, the crystals of which having been quickly formed are small and subside on being left at rest as a fine crystalline precipitate.

On gradually warming the felted mass much more rapid transformation takes place, the needle-shaped crystals crumble away, while a shower of small well-shaped rhombic crystals falls to the bottom of the beaker. In the appended plate, Fig. 1 shows a beaker, about half its natural size, filled with a felted mass of needles of the



hexahydrated modification immediately after crystallization had taken place. Fig. 2 shows the same beaker 24 hours later after complete transformation of the hexahydrated into the tetrahydrated modification had occurred.

If solutions of lower concentration than  $0.2\ N$  are mixed, the deposition of the needle-shaped crystals is slower and they are consequently larger in size. Fig. 3 shows a cluster of such crystals about the natural size which separated on mixing one-fifteenth normal solutions and Fig. 4 shows the same cluster after 24 hours when partial transformation had occurred.

When normal solutions of potassium sodium tartrate and calcium chloride are mixed, a slightly flocculent precipitate is at once formed which becomes denser and definitely crystalline as the small needles increase in size. Half normal solutions show the same appearance, the original precipitate being, however, less in amount. When one-third normal solutions are mixed the initial precipitate is very slight while with  $0.02\ N$  solutions, as above described, the mixed liquid remains clear for a short time until the tufts of needles appear.

The needle-shaped modification which first separates contains 6 molecules of water of crystallization, two of which are



Fig. 3.



Fig. 4.

lost during transformation. For purposes of analysis the hexahydrated crystals prepared as above described by mixing equal amounts of 0.2 *N* solutions of calcium chloride and potassium sodium tartrate were separated by filtration, using a water pump, and thoroughly washed on the filter with distilled water. They were then quickly washed twice with alcohol and once with ether and rapidly pressed between filter paper. The last traces of adhering moisture were removed by exposing them for five minutes over calcium chloride in a vacuum desiccator.

The new form was thus obtained as very fine, colorless needles. When exposed to the air, water was slowly given off, and a crystalline powder of the tetrahydrated form was obtained. When left in a stoppered bottle transformation slowly took place, the crystals became moist, and water was given off which bedewed the sides of the bottle, a crystalline powder of the tetrahydrated form again being produced.

Transformation and loss of water is more rapid at a slightly raised temperature. At the ordinary temperature three or four days' exposure to the air is required before transformation is complete and the weight constant, while at 40° only a few hours' exposure are needed. The crystals of the tetrahydrated form can be heated to 60° in a current of air without any appreciable loss of weight. The loss of water during transformation was estimated by exposing a weighed quantity of the needle-shaped modification to the air until its weight remained constant.

1.5522 lost 0.1884 of water. Loss of water = 12.13%.

The calcium in the needle-shaped modification was estimated by igniting a weighed amount in the air and weighing the calcium oxide obtained.

1.1717 g. gave 0.2227 of calcium oxide.  $\text{Ca} = 13.58\%$

$\text{C}_4\text{H}_4\text{O}_6\text{Ca}_2\cdot 6\text{H}_2\text{O}$  requires loss of  $2\text{H}_2\text{O} = 12.16\%$ .  $\text{Ca} = 13.52\%$

Mr. T. V. Barker, to whom the thanks of the author are due, has measured some crystals of the orthorhombic tetrahydrated modification obtained by the slow transformation of the hexahydrated form. He found them to be crystallographically identical with those successively examined by Pasteur,<sup>1</sup> by Rammelsberg,<sup>2</sup> and by Hintze.<sup>3</sup>

In confirmation of the work of these observers no hemihedral facets were observed but, as Pasteur notes, absence of geometrical enantio-morphism does not necessarily preclude asymmetry of structure.

The new hexahydrated modification crystallizes in long, very slender, doubly refracting needles with straight extinction and is not suitable for goniometrical examination.

OXFORD, ENGLAND.

<sup>1</sup> *Ann. chim. phys.*, [3] 24, 449 (1848).

<sup>2</sup> *Kryst. Phys. Chemie, Abt. II*, 136.

<sup>3</sup> *Ann.*, 226, 301 (1884).

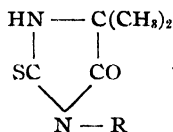
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TEXAS.]

THE 5,5-DIMETHYL-3-R-2-THIOHYDANTOINS.<sup>1</sup>

By J. R. BAILEY AND A. T. McPHERSON.

Received May 19, 1916.

In the year 1908, Bailey and Randolph published in the *Berichte* of the German Chemical Society an article entitled "Kritische Bemerkungen zu einer Abhandlung von W. Marckwald, M. Neumark and R. Stelzner: Ueber Thiohydantoine und von diesen derivierende Basen."<sup>2</sup> In working out methods for the desulfurization of thiohydantoins,<sup>3</sup> Bailey and Randolph had occasion to prepare certain 5,5-dimethyl-3-R-2-thiohydantoins of the general formula



where R represents an alkyl or an aryl.

In the table below is given a list of the substances described in the article of Marckwald, Neumark and Stelzner, "Ueber Thiohydantoine und von diesen derivierende Basen,"<sup>4</sup> which were later prepared by Bailey and Randolph. The compounds in the article of the German investigators, which were under criticism by Bailey and Randolph, as well as the additional substances which are discussed in the present paper, were contributed to the article of Marckwald, Neumark and Stelzner by Dr. Stelzner, at the time a co-worker of Prof. Marckwald. A comparison of the melting points of the substances, obtained by Stelzner on the one hand and by Bailey and Randolph on the other hand, indicates beyond any doubt that the compounds, obtained in these two investigations and to which are ascribed the same constitution, are not identical.

	Melting points.	
	By Stelzner.	By Bailey and Randolph.
(a) 3,5,5-Trimethyl-2-thiohydantoin.....	53°	145°
(b) 5,5-Dimethyl-3-phenyl-2-thiohydantoin....	67°	174°
(c) Methyl ether of "b".....	Zähflüssiges helles Liquidum	96°
(d) Platinum salt of "c".....	132°	240°
(e) Picrate of "c".....	174°	194°
(f) 5,5-Dimethyl-3- <i>p</i> -tolyl-2-thiohydantoin....	85°	223°

In regard to the results tabulated above, Bailey and Randolph made the following statement:

<sup>1</sup> This paper was sent to Dr. Stelzner in May for his criticism but no reply has been received. Because of the uncertainty of mails to Germany at the present time it does not seem best to wait longer before publication.—EDITOR.

<sup>2</sup> *Ber.*, 41, 2505 (1908).

<sup>3</sup> *Ibid.*, 41, 2494 (1908).

<sup>4</sup> *Ber.*, 24, 3278 (1891).

"Da nun aus den Ergebnissen unserer Mitteilung über die Entschwefelung von Thiohydantoinen mit grösster Wahrscheinlichkeit zu folgern ist, dass wir die wirklichen Thiohydantoine erhalten haben, so kann die von Stelzner den betreffenden Verbindungen zugesprochene Konstitutionsformel nicht zutreffend sein. Welche Formel die in Rede stehenden Substanzen in Wirklichkeit besitzen, haben wir nicht ermitteln können. Da bei den betreffenden Versuchen stets eine alkoholische Lösung der Senföle benutzt wurde, so drängte sich uns der Gedanke auf, dass die von Stelzner beschriebenen



Derivate vielleicht Thiourethane,  $\text{C}_2\text{H}_5\text{OCNH} - \text{R}$ , waren, die irrtümlicherweise für Thiohydantoine gehalten worden sind. Dieser Annahme steht jedoch die Thatsache entgegen, dass die Analysenresultate Stelznerns die in den meisten Fällen die Bestimmung von Kohlenstoff, Wasserstoff, Stickstoff und Schwefel umfassen, gut auf die Thiohydantoin-Formel stimmen. Da die in unseren beiderseitigen Beobachtungen zutage getretenen Differenzen kaum auf Tautomerie zurückgeführt werden können, so muss es sich um eine Isomerie handeln, deren Aufklärung noch aussteht."

The substances obtained by Stelzner are now given in Richter's "Lexikon der Kohlenstoffverbindungen" as *isomers* of the Bailey and Randolph compounds. However, Dr. Stelzner has, since the publication of the Bailey and Randolph article, worked over the ground and writes:

"Wie Sie bereits richtig vermuteten, beziehen sich die von mir herrührenden Schmelzpunktsangaben auf die bei der Kondensation von Aminosäuren mit Senfölen bei Gegenwart von alkoholischen Kali gleichzeitig oder vielleicht richtiger zunächst entstehenden Thiourethane.....meine Analysenzahlen aber sich auf die Thiohydantoine." In justice to Dr. Stelzner his explanation should be quoted of "der ganz merkwürdige Zufall dass die in der Bruttoformel so gänzlich verschiedenen Thiourethane und Thiohydantoine in der prozentualen Zusammensetzung sich einander recht nahe stehen, und dementsprechend auch die teils von mir, teils von anderer Seite ausgeführten Analysen keinen Hinweis auf die in meinen Thiohydantoinen zweifellos noch vorhandenen Verunreinigungen gaben."

In whatever way the errors in Stelzner's work may be accounted for, it is simply our aim in the present article to direct attention to the fact that none of the supposed 5,5-dimethyl-3-R-2-thiohydantoins or their derivatives, described in the article referred to above, were obtained by Stelzner—at least in a form approximating purity.

As *o*-tolyl-dimethylthiohydantoin and some derivatives of this are also described by Stelzner in the article referred to above, it seemed desirable that this work also be investigated. Here again products have been obtained that do not correspond in their melting points with the results obtained by Stelzner, as is evident from the following tabulated comparison:

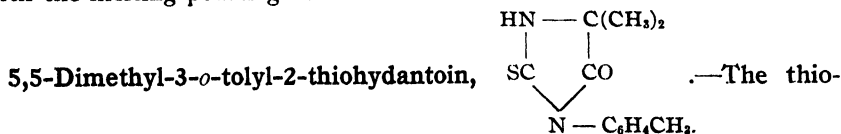
	Melting points.	
	By Stelzner.	By Bailey and McPherson.
(a) 5,5-Dimethyl-3- <i>o</i> -tolyl-2-thiohydantoin.	175°	195.5°
(b) Methyl ether of "a".....	Schmilzt bei Zimmertemperatur	75°
(c) Platinum salt of "b".....	No data	220°
(d) Sulfate of "b".....	208°	196°
(e) Picrate of "b".....	212°	152°

There is no possibility that Stelzner was confused in the work on the *o*-tolyl derivatives by the presence of *o*-tolylthiourethane, because the latter substance is described in the literature as a liquid. It is true that, as shown in the experimental part of this article, this thiourethane, when pure, is a crystalline solid at room temperature, but in its preparation a liquid is always obtained and considerable care must be exercised in its preparation to effect crystallization.

In justice to Dr. Stelzner, attention should be directed to the fact that at the time he carried out his work  $\alpha$ -aminoisobutyric acid was a substance difficult to prepare and the sulfate with which he worked might have been contaminated with ammonium sulfate. There is some probability of this, in view of the fact that he assigned to this salt the formula  $(\text{CH}_3)_2\text{C}(\text{NH}_2)\text{COOH} \cdot \text{H}_2\text{SO}_4$ . Bailey and Randolph showed the formula of the normal salt to be  $[(\text{CH}_3)_2\text{C}(\text{NH}_2)\text{COOH}]_2 \cdot \text{H}_2\text{SO}_4$ . Experiments have convinced us that Stelzner's acid salt can be prepared, but it will not stand recrystallization from water as stated by Stelzner.

#### Experimental Part.

The  $\alpha$ -aminoisobutyric acid used in this work was prepared according to the method of Gulewitsch.<sup>1</sup> The *o*-tolyl mustard oil, made from *o*-toluidine, boiled at  $238^\circ$  at 744 mm. The boiling point given by Mainzer<sup>2</sup> is  $237^\circ$ . As a further confirmation of the purity of the mustard oil, the following derivatives were made:  $o\text{-CH}_3\text{C}_6\text{H}_4\text{NHCSNH}_2$ ,  $o\text{-CH}_3\text{C}_6\text{H}_4\text{-NHCSNHC}_6\text{H}_5$ , and  $(o\text{-CH}_3\text{C}_6\text{H}_4\text{NH})_2\text{CS}$ . These preparations melted at  $159^\circ$ ,  $139.5^\circ$ , and  $158.5^\circ$ , respectively, which data stand in accord with the melting points given in Beilstein for these substances.



hydantoin is readily prepared according to the method of Marckwald, Neumark and Stelzner,<sup>3</sup> as follows: An alcoholic solution of equimolecular amounts of *o*-tolyl mustard oil and potassium aminoisobutyrate is boiled one hour, the alcohol distilled off, the residue taken up with water, and then the thiohydantoin precipitated by the addition of hydrochloric acid. Our preparation, purified by recrystallization from dilute alcohol and then from benzene, melted at  $195.5^\circ$  without decomposition. From benzene the thiohydantoin crystallizes in short, thick, microscopic prisms without end faces.

Calc. for  $\text{C}_{12}\text{H}_{14}\text{ON}_2\text{S}$ : C, 61.54%; H, 5.98%; N, 11.97%; S, 13.67%.

Found: C, 61.69; H, 6.19; N, 12.03; S, 13.92.

<sup>1</sup> *Ber.*, **39**, 1184 (1906).

<sup>2</sup> *Ibid.*, **15**, 1413 (1882).

<sup>3</sup> *Ibid.*, **24**, 3280 (1891).

**5,5-Dimethyl-3-*o*-tolylhydantoin.**—As a proof of the constitution of the above thiohydantoin, it was desulfurized with bromine by the method of Bailey and Randolph.<sup>1</sup> The new substance thus obtained crystallizes from a benzene-petrolie ether mixture in the form of characteristic, thin, prismatic plates, melting at 172° undecomposed.

Calc. for  $C_{12}H_{14}O_2N_2$ : C, 66.06%; H, 6.42%; N, 12.84%.

Found: C, 66.16; H, 6.61; N, 12.62.

**Methyl Ether of 5,5-Dimethyl-3-*o*-tolyl-2-thiohydantoin.**—The methyl ether was prepared according to the method of Marckwald, Neumark and Stelzner by boiling an alcoholic solution of the thiohydantoin with a slight excess of methyl iodide in the presence of one mol of potassium hydroxide until the solution was neutral to litmus. On recrystallization from petrolie ether, it is obtained in the form of short prisms, which melt undecomposed at 75°.

Calc. for  $C_{12}H_{16}ON_2S$ : C, 62.90%; H, 6.45%; N, 11.29%; S, 12.91%.

Found: C, 63.05; H, 6.56; N, 11.47; S, 12.87.

**Picrate of the Methyl Ether.**—The picrate separates in thin, yellow plates on the addition of picric acid to an alcoholic solution of the methyl ether. After recrystallization from alcohol, it melts with decomposition at 152°.

Calc. for  $C_{19}H_{19}O_8N_3S$ : N, 14.68%. Found: N, 14.75.

**Platinum Salt of the Methyl Ether.**—On the addition of platinic chloride to a solution of the methyl ether in dilute hydrochloric acid, an oil separates which, on standing a short time, changes to an orange-red, crystalline solid. Purification is effected by washing with water and with petrolie ether. On rapid heating this substance melts with complete decomposition at 220°.

Calc. for  $C_{26}H_{34}O_4N_4S_2PtCl_6$ : Pt, 21.57%. Found: Pt, 21.50.

**Sulfate of the Methyl Ether.**—The methyl ether is dissolved in the calculated amount of sulfuric acid in alcohol and the sulfate then precipitated with dry ether. The substance purified by several precipitations from alcoholic solution with ether, is obtained in the form of slender, microscopic prisms and melts at 196°.

Calc. for  $C_{12}H_{18}O_6N_2S_2$ : S, 18.51%. Found: S, 18.35.

***o*-Tolylthiourethane,  $CH_3C_6H_4NHCSOC_2H_5$ .**—*o*-Tolylthiourethane prepared by Schiff's method<sup>2</sup> is obtained as an oil, which does not solidify in a freezing mixture, and is so described by Liebermann and Natanson.<sup>3</sup> However, either on being dried over fused chloride of calcium, or after long standing, it changes to a crystalline solid. Furthermore, if the oil be dissolved in petrolie ether, the solution strongly cooled, and then

<sup>1</sup> *Ber.*, 41, 2497 (1908).

<sup>2</sup> *Ibid.*, 9, 1316 (1876).

<sup>3</sup> *Ann.*, 207, 161 (1881).

a crystal of the substance added, the thiourethane separates in thin prismatic plates. It melts at 37° apparently undecomposed.

Calc. for  $C_{10}H_{15}ONS$ : C, 61.52%; H, 6.66%; N, 7.18%; S, 16.43%.

Found: C, 61.37; H, 6.84; N, 7.31; S, 16.42.

AUSTIN, TEXAS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE MICHIGAN AGRICULTURAL COLLEGE.]

## ACTION OF AROMATIC ALCOHOLS ON AROMATIC COMPOUNDS IN THE PRESENCE OF ALUMINUM CHLORIDE. I.

BY RALPH C. HUSTON AND THEODORE E. FRIEDMANN.

Received September 16, 1916.

The condensation of aromatic alcohols with aromatic compounds to form derivatives of di- or triphenylmethane is commonly brought about by the following dehydrating agents: sulfuric acid,<sup>1</sup> phosphorus pentoxide,<sup>2</sup> zinc chloride,<sup>3</sup> dilute or concentrated hydrochloric acid,<sup>4</sup> sulfuric and acetic acids,<sup>5</sup> absolute alcohol,<sup>6</sup> stannic chloride,<sup>7</sup> and acetic acid.<sup>8</sup>

Aluminum chloride has been used as a dehydrating agent in organic chemistry by Merz and Weith,<sup>9</sup> Sholl and Seer,<sup>10</sup> Wass,<sup>11</sup> Graebe,<sup>12</sup> Jaubert,<sup>13</sup> Frankforter and Kritchevsky,<sup>14</sup> Frankforter and Kokatnur,<sup>15</sup> and others.<sup>16</sup>

We do not find, however, a record of the dehydrating action of aluminum chloride on aromatic alcohols and aromatic compounds. This preliminary

<sup>1</sup> Myer and Wurster, *Ber.*, **6**, 964 (1873); Becker, *Ibid.*, **15**, 2091 (1882); Noelting, *Ibid.*, **24**, 3127, 3136 (1891); Gatterman and Koppert, *Ibid.*, **26**, 2811 (1893); Bistrzycki and Plateau, *Ibid.*, **28**, 989 (1895); Pritsch, *Ibid.*, **29**, 2300 (1896); Bistrzycki and Simonis, *Ibid.*, **31**, 2812 (1898), etc.

<sup>2</sup> Hemilian, *Ber.*, **7**, 1203 (1874); Michael and Jeanpretre, *Ibid.*, **25**, 1615 (1892), etc.

<sup>3</sup> Fischer and Roser, *Ber.*, **13**, 674 (1879); *Ann.*, **206**, 113, 155 (1880); Liebmann, *Ber.*, **15**, 152 (1882); Kippenberg, *Ibid.*, **30**, 1140 (1897), etc.

<sup>4</sup> Suais, *Bull.*, [3] **17**, 517 (1897); D. R. P. 27032; Noelting, *Ber.*, **24**, 3127 (1891); Noelting, *Ibid.*, **24**, 553 (1891), etc.

<sup>5</sup> Paterno and Fileti, *Gazz.*, **5**, 381 (1875); Mohlau and Klöpfer, *Ber.*, **32**, 2147, 2149 (1899).

<sup>6</sup> Möhlau and Klöpfer, *Ber.*, **32**, 2150, 2153 (1899).

<sup>7</sup> Bistrzycki, *Ibid.*, **37**, 659 (1904).

<sup>8</sup> Khotinski and Potzewitch, *Ibid.*, **42**, 3104 (1909).

<sup>9</sup> *Ber.*, **14**, 189 (1881).

<sup>10</sup> *Ann.*, **394**, 119 (1912).

<sup>11</sup> *Ber.*, **15**, 1128 (1882).

<sup>12</sup> *Chem. Ztg.*, **25**, 268 (1901); *Ber.*, **34**, 1778 (1901).

<sup>13</sup> *Compt. rend.*, **132**, 841 (1901).

<sup>14</sup> *This Journal*, **36**, 1511 (1914); **37**, 385 (1915).

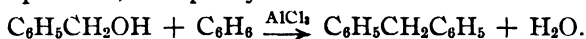
<sup>15</sup> *Ibid.*, **36**, 1529 (1914).

<sup>16</sup> *Ber.*, **40**, 1694 (1907); D. R. P. 136,015, etc.

paper is the first of a series of articles which we hope to publish on this field.

When benzyl alcohol was mixed with a little more than the molecular equivalent of benzene, and the mixture treated with anhydrous aluminum chloride, a rather vigorous reaction took place. Heat and hydrochloric acid were evolved, and the mass became dark colored and pasty. After decomposing with ice water, and extracting with ether five compounds were isolated by fractional distillation.

The product formed in the largest amount (30% theory) boiled, after redistillation at 262–264°. It was identified further by analysis and oxidation to benzophenone, as diphenylmethane.



The residue was distilled under 30 mm. pressure until the temperature rose to 350°. This distillate was then separated by fractionation at 20 mm. into two portions, which came over between 250° and 265° and between 308° and 316°, respectively. The first of these consisted chiefly of *p*-dibenzylbenzene (8% theory) together with a little *o*-dibenzylbenzene, and an oily impurity. The *p*-dibenzylbenzene was identified by melting point, analysis, bromination and oxidation to *p*-dibenzoylbenzene; the *o*-dibenzylbenzene by its melting point.

The fraction which came over at 308–316° at 20 mm. has the formula, as indicated by analysis and molecular weight determination,  $\text{C}_{27}\text{H}_{24}$ . It is probably either tribenzylbenzene,  $\text{C}_6\text{H}_3(\text{CH}_2\text{C}_6\text{H}_5)_3$ , or methylene-*bis*-diphenylmethane,  $\text{C}_6\text{H}_5\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_5$ . A subsequent paper will contain a more complete description of this compound.

The residue from the vacuum distillation was distilled at ordinary pressure and yielded about 20% of the theoretically possible amount of crude anthracene. This was purified by sublimation and oxidized to anthraquinone.

The yields of the products are greatly influenced by the amounts of the reagents used, and the temperature at which the reaction is carried out. In one experiment where the temperature was kept below 35° and a large excess (5.2 mols) of benzene was used, the diphenylmethane almost equaled in weight the benzyl alcohol taken. Conditions which gave large yields of diphenylmethane gave small yields of anthracene.

Schramm<sup>1</sup> and Radziewanowski<sup>2</sup> found that this same rule held when benzylchloride and benzene react in the presence of  $\text{AlCl}_3$ .

Verley<sup>3</sup> (working under reduced pressure) prepared diphenylmethane from chloromethylethyl ether, benzene, and aluminum chloride. Since he obtained evidence of a small amount of benzylethyl ether in the reac-

<sup>1</sup> *Ber.*, 26, 1706 (1893).

<sup>2</sup> *Ibid.*, 27, 3237 (1894).

<sup>3</sup> *Bull.*, [3] 17, 914 (1897).



tion mixture, he assumed that the reaction takes place in three steps: First, the chloromethylethyl ether reacts with benzene to give benzylethyl ether,  $\text{C}_6\text{H}_6 + \text{ClCH}_2\text{OC}_2\text{H}_5 \xrightarrow{\text{AlCl}_3} \text{C}_6\text{H}_5\text{CH}_2\text{OC}_2\text{H}_5 + \text{HCl}$ . Second, the ether thus formed reacts with hydrochloric acid to form benzyl chloride and alcohol,  $\text{C}_6\text{H}_5\text{CH}_2\text{OC}_2\text{H}_5 + \text{HCl} \longrightarrow \text{C}_6\text{H}_5\text{CH}_2\text{Cl} + \text{C}_2\text{H}_5\text{OH}$ . Third, the benzyl chloride then reacts with a second molecule of benzene to give diphenylmethane,  $\text{C}_6\text{H}_5\text{CH}_2\text{Cl} + \text{C}_6\text{H}_6 \xrightarrow{\text{AlCl}_3} \text{C}_6\text{H}_5\text{CH}_2\text{C}_6\text{H}_5 + \text{HCl}$ .

In the light of this explanation we thought it of interest to determine the effect of aluminum chloride on a mixture of benzylethyl ether and benzene. The ethyl ether of benzyl alcohol when mixed with  $1\frac{2}{3}$  mols benzene and treated with  $\text{AlCl}_3$  reacted much less readily than did benzyl alcohol under the same conditions. The products of the reaction were the same<sup>1</sup> but the yields were much smaller. The reaction mixture yielded, after standing more than a week, about 15% of unchanged benzylethyl ether.

If the hypothesis of Verley is correct and if benzylethyl ether is fairly stable in the presence of benzene and aluminum chloride, one would expect to obtain a considerable amount of benzylethyl ether from the reaction mixture when chloromethylethyl ether is treated with benzene and aluminum chloride. An experiment was made with the conditions comparable to those of the preceding experiment. The reaction was much more vigorous and seemed to be complete at the end of two days. A great deal more anthracene was formed as compared to the diphenylmethane than was the case when either benzyl alcohol or benzylethyl ether was used. We were unable to obtain *any* benzylethyl ether from the reaction mixture.

These results led us to try the effect of an excess of aluminum chloride on chloromethylethyl ether alone. A vigorous reaction set in and hydrochloric acid was given off. After standing overnight (protected from moisture by  $\text{CaCl}_2$ ) the mixture was decomposed with ice water. A volatile oil separated out and the odor of formaldehyde was quite distinct.

While these experiments are not conclusive, they lead us to suggest an alternate explanation for the action of aluminum chloride on a mixture of chloromethylethyl ether and benzene. We suggest that the ether is first decomposed by the aluminum chloride to form formaldehyde,<sup>2</sup> which then reacts with benzene to form diphenylmethane and anthracene. It is quite possible that both reactions occur simultaneously, but the large amount of anthracene formed,<sup>3</sup> and the absence of an appreciable amount of benzylethyl ether both point to the second hypothesis.

<sup>1</sup> Meyer (*J. prakt. Chem.*, [ii] 82, 538 (1910)) has shown that  $\text{P}_2\text{O}_5$  acts on benzylethyl ether and benzene to give diphenylmethane.

<sup>2</sup> Compare with the findings of Waas, *Ber.*, 15, 1128 (1882).

<sup>3</sup> Frankforter and Kokatnur (*loc. cit.*) have shown that formaldehyde benzene and aluminum chloride yield a large amount of anthracene.

We are unable at the present time to throw much light on the mechanism of the reaction between aromatic alcohols, aromatic compounds and aluminum chloride. We hope to be able to explain it more fully in future papers. Our work, thus far, has shown the formation of an intermediate product which resembles the intermediate product formed in Friedel and Kraft's reaction. A rather large proportion of  $\text{AlCl}_3$  is necessary for the production of a good yield of diphenylmethane.

It may be that a further study of this reaction will help to give an insight into the mechanism of the reaction between aldehydes, aromatic compounds and aluminum chloride.<sup>1</sup>

### Experimental.

**Benzyl Alcohol, Benzene and Aluminum Chloride, I.**—Fifty-five grams of benzyl alcohol (freshly prepared from benzaldehyde and free from chlorine) were added to 50 g. of benzene. The mixture was cooled and stirred constantly with a motor. Aluminum chloride was added in small portions until a total of 40 g. had been added. The temperature was kept at 30–35° except for a brief period when it rose to 55°. Much hydrochloric acid was evolved and the mixture became dark colored, pasty and fluorescent. It was allowed to stand at room temperature for ten days, and was then decomposed with ice water and extracted with ether. The ether extract was dried over  $\text{CaCl}_2$ . Most of the ether was driven off and the residue was fractionated.

#### Second Fractionation.

60–130°, 12.5 g. (mostly benzene); 130–240°, 0.7 g.; 240–280°, 25.5 g.

The pressure was reduced to 30 mm. and the distillation continued until nothing more would come over under 350°. The distillate weighed 20 g. This was subjected to fractionation at 20 mm.

#### Second Fractionation.

245–265°, 10.5 g.; 265–305°, 1.5 g.; 308–316°, 5.27 g.

The residue (15 g.) was distilled at ordinary pressure, until the flask melted and nothing more would come over. 8.5 g. of a yellow oil came over and solidified in the receiver.

The fraction which came over at 240–280° at ordinary pressure had after repeated distillation, a constant boiling point of 262–264°. 20 g. of it yielded 14 g. of benzophenone when oxidized with potassium dichromate, and sulfuric acid.<sup>2</sup> An analysis gave the following:

0.1708 g. subst. gave 0.5802 g.  $\text{CO}_2$  and 0.1127 g.  $\text{H}_2\text{O}$ .

Calc. for  $\text{C}_{18}\text{H}_{12}$ : C, 92.8%; H, 7.2%. Found: C, 92.58%; H, 7.39%.

The substance is, therefore, diphenylmethane.

The fraction which came over at 245–265° at 20 mm. was redistilled.

<sup>1</sup> See Dinesmann, *Compt. rend.*, **141**, 201 (1905); and Frankforter and Kritchevsky, *THIS JOURNAL*, **36**, 1511 (1914); **37**, 385 (1915).

<sup>2</sup> Zincke, *Ann.*, **159**, 377 (1871).

Most of it came over between 252–255°. On standing overnight the larger part of it crystallized. It was cooled and filtered at the pump. The crystals were dried between filter papers and recrystallized alternately from alcohol and ether. 5.3 g. of colorless plates melting at 85–86° were obtained. 1 g. of these when oxidized with 2 g. of  $\text{CrO}_3$  in acetic acid gave 0.8 g. of *p*-dibenzoyl benzene, melting at 159–160°. Another 1 g. portion was brominated in chloroform solution.<sup>2</sup> A dibromide was obtained which melted, after repeated recrystallization, from petroleum, ether and benzene, at 112.5°. An analysis of the hydrocarbon gave:

0.1826 g. subst. gave 0.6247 g.  $\text{CO}_2$  and 0.1142 g.  $\text{H}_2\text{O}$ .

Calc. for  $\text{C}_{20}\text{H}_{18}$ : C, 92.97%; H, 7.03%. Found: C, 93.29%; H, 7.01%.

It is, therefore, *p*-dibenzylbenzene,  $\text{C}_6\text{H}_5\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_5$ .

From the combined filtrates of the *p*-dibenzylbenzene, a small amount (0.7 g.) of *o*-dibenzylbenzene melting at 78° was obtained.

The fraction which came over at 308–316° at 20 mm. was redistilled. Most of it came over between 312° and 314°. An analysis and molecular weight determination indicated the formula  $\text{C}_{27}\text{H}_{24}$ .

0.2067 g. and 0.1998 g. of subst. gave 0.702 g. and 0.6807 g.  $\text{CO}_2$ , and 0.1275 g. and 0.1284 g.  $\text{H}_2\text{O}$ .

Calc. for  $\text{C}_{27}\text{H}_{24}$ : C, 93.05%; H, 6.95%. Found: C, 92.64%, 92.91%; H, 6.91%, 7.19%.

Calculated molecular weight, 348.2. Found: 342.4 and 354.

The yellow solid which was obtained by heating the residue after the vacuum distillation was freed from oil by means of a porous plate, crystallized from benzene and alcohol and sublimed. The sublimate had the characteristic appearance of anthracene. It melted sharply at 212–213°. 2 g. were oxidized with chromium trioxide and acetic acid. After recrystallization from glacial acetic acid the resulting fine needles melted at the correct temperature for anthraquinone, 276–277°.

**Benzyl Alcohol, Benzene and Aluminum Chloride, II.**—Fifty grams of benzyl alcohol were added to 200 g. benzene and treated with 35 g. aluminum chloride in small portions. The temperature was easily kept between 30° and 35°. The mixture turned reddish brown and gave off hydrochloric acid. After five days it was poured into ice water. The aqueous portion was separated from the benzene portion and extracted with ether. Most of the ether was driven from the extract and the residue was added to the benzene portion. This was dried over  $\text{CaCl}_2$  and subjected to fractionation.

#### Second Fractionation

60–110°, 142 g. (benzene); 110–235°, 4 g.; 235–280°, 46.5 g.

The pressure was reduced to 30 mm. and the distillation continued to 350°. 11.5 g. came over. This was refractionated at 20 mm.

<sup>1</sup> Zincke, *Ber.*, **9**, 31 (1876).

<sup>2</sup> Thiele and Balhorn, *Ibid.*, **37**, 1467 (1904).

## Second Fractionation.

245–265°, 7.5 g.; 265–305°, 1 g.; 308–316°, 2.5 g.

The small amount of residue (2.5 g.) was heated under atmospheric pressure. About 1 g. of crude anthracene was obtained.

These fractions yielded, on purification:

Diphenylmethane.....	44.5 g.
<i>p</i> -Dibenzyl benzene.....	4.2 g.
<i>o</i> -Dibenzyl benzene.....	0.5 g.
Hydrocarbon, C <sub>27</sub> H <sub>24</sub> .....	2.0 g.
Anthracene.....	0.6 g.

**Benzylethyl Ether,<sup>1</sup> Benzene and Aluminum Chloride.**—Fifty grams of the ether were mixed with an equal weight of benzene and stirred while 40 g. of aluminum chloride were added in small portions. Cooling was omitted. The temperature rose to about 45°. Hydrochloric acid was given off and the mixture became dark colored. The reaction was quite slow, hydrochloric acid being evolved in considerable amount for about a week. After ten days the mass was decomposed with ice water, extracted with ether, dried and distilled.

## Second Fractionation.

60–110°, 18 g. (benzene); 110–220°, 7.5 g.; 220–280°, 9 g.; 240–350° (30 mm.), 6 g.

The residue distilled at atmospheric pressure yielded 4 g. of crude anthracene.

Most of the fraction from 110° to 220° boiled at 178–182°. It was identified as unchanged benzylethyl ether. The fraction from 220° to 280° was crude diphenylmethane. The fraction from 240° to 350° (30 mm.) yielded 2 g. of *p*-dibenzyl benzene, 0.3 g. *o*-dibenzyl benzene, and about 1 g. of the hydrocarbon C<sub>27</sub>H<sub>24</sub>.

**Chloromethylethyl Ether, Benzene and Aluminum Chloride.**—Thirty-five grams of freshly prepared chloromethylethyl ether were dissolved in 75 g. of benzene, and treated with 35 g. of aluminum chloride. The reaction was quite violent. Although the aluminum chloride was added very slowly and the mixture well cooled, the temperature rose to 43°. Hydrochloric acid was evolved rapidly. The mixture turned red, then reddish brown and became rather pasty. After three days it was decomposed with ice water and extracted with ether. A small amount (2 g.) of a yellow precipitate remained undissolved and was filtered off. This was not investigated. The ether extract was dried over CaCl<sub>2</sub> and distilled.

## Second Fractionation.

60–120°, 12 g. (benzene); 120–220°, 0.5 g.; 220–280°, 9.8 g.; 235–350° (30 mm.), 2.5 g.

Twelve grams crude anthracene were obtained from the residue.

<sup>1</sup> This ether was freshly prepared from benzyl chloride and sodium ethylate. It gave a faint cloudiness when tested for chlorine.

The thermometer rose rapidly from  $120^{\circ}$  to  $220^{\circ}$ . No evidence of benzyl-ethyl ether was found. The fraction from  $220^{\circ}$  to  $280^{\circ}$  was identified as diphenylmethane. No investigation was made for the oil which came over between  $235^{\circ}$  and  $350^{\circ}$  at 30 mm.

**Chloromethylethyl Ether and Aluminum Chloride.**—Fourteen grams of chloromethylethyl ether were placed in a flask fitted with a calcium chloride tube and treated with an excess (22 g.) of aluminum chloride in small amounts. A vigorous reaction set in, heat was evolved, and hydrochloric acid was given off rapidly. After standing overnight, all reaction seemed to have ceased. The flask contained a reddish brown syrup and some unchanged aluminum chloride. The whole was poured into ice water. A small amount of volatile oil came to the surface. The aqueous solution smelled strongly of formaldehyde. A portion was just neutralized with NaOH and filtered. A piece of filter paper, moistened with ammoniacal silver nitrate solution, was turned black when held over the warmed filtrate.

EAST LANSING, MICH.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF BRYN MAWR COLLEGE.]

## THE MOLECULAR WEIGHT OF SOME ALCOHOLATES OF CHLORAL AND BUTYLCHLORAL IN BENZENE SOLUTION.

BY MARGUERITE WILLCOX AND ROGER F. BRUNEL.

Received September 16, 1916.

The partial dissociation of chloralethylalcoholate into its constituents when dissolved in organic solvents, first investigated by Beckman,<sup>1</sup> was more extensively examined by Willcox and Brunel in a recent article,<sup>2</sup> in connection with an investigation of the replacement of one alcohol by another in such alcoholates. It has now been found that other alcoholates of chloral and butylchloral are likewise, as would be expected, somewhat dissociated in solution.

An examination of Table II, p. 1827, in the above paper by the authors, and of the reactions on which it is based, make evident certain conclusions as to the relative tendency to dissociation which these alcoholates of various alcohols should exhibit. It is there concluded that as we pass downward in the table, in the list of alcohols there studied, the affinity of the alkyl groups for the hydroxyl becomes relatively greater than their affinity for the chloral and butylchloral radicals. The tendency of the alcohols to form alcoholates with the aldehydes, involving separation of the alkyl group from the hydroxyl, should, therefore, decrease in this order, so that the degree of dissociation of the alcoholates should increase as we pass downward in the list of alcohols in this table. The following experiments show

<sup>1</sup> *Z. physik. Chem.*, 2, 724 (1888).

<sup>2</sup> *THIS JOURNAL*, 38, 1821 (1916).

this to be the case, the alcoholates of primary alcohols being least highly, those of tertiary alcohols most highly dissociated, with those of secondary alcohols falling between them. The concentrations are not the same for all of them, but are sufficiently close to make the relationship clear.

The purest benzene obtainable was frozen out four times, dried with calcium chloride and phosphorus pentoxide, and distilled. B. p. 79.4. The value 4.9 was used for the constant. The concentrations are given in per cent. by weight.<sup>1</sup>

Solute.	$\Delta$ .	Per cent. conc.	Mol. wt.		Per cent. dissociation.
			Calc.	Found.	
Chloroethylalcoholate.....	0.543°	2.00	193	189	2.30
	1.276	4.77		197	Assocd.
Chloral- <i>l</i> -amylalcoholate.....	1.547	6.815	235	232	1.29
	1.539	6.812		232	1.29
Chloral methylpropylcarbinolate..	1.440	6.21	235	225	4.00
Chloral- <i>l</i> -amylalcoholate.....	1.460	5.94	235	212	10.8
Butylchloroethylalcoholate.....	1.728	6.82	221	208	6.25
	2.945	12.38		235	Assocd.
Butylchloral-sec.butylalcoholate...	1.087	4.41	250	208	20.2
	2.167	8.976		223	12.0
Butylchloral- <i>l</i> -amylalcoholate.....	2.715	6.29	264	198	33.3

If some of these more highly dissociated alcoholates underwent some dissociation in the equilibrium experiments of the earlier paper by the authors, above referred to, it would have to be taken into account in order to determine the true equilibrium between the molecular forms of the alcoholates. A little consideration will show that it could not affect the order in which the alcohols would fall in the series there studied, but would merely accentuate the differences in the end points which would be found if the dissociation were negligible in amount.

It cannot be stated with certainty whether or not such dissociation occurred. The concentration of the tertiary alcoholates fell, in the chloral series, as low as 2 g., that of butylchloral-*d*-sec.butylalcoholate in some cases as low as 9 g. per hundred cc. of solution. Expressed as per cent. by weight both of these values would be somewhat higher. These are concentrations at which the alcoholates concerned should be somewhat dissociated. But it must be kept in mind that there were always two such alcoholates present when equilibrium was reached giving a common dissociation product, and it is reasonable to assume that some suppression of the dissociation of each would occur. If we assume that we may apply the principle frequently employed in the case of electrolytic dissociation, according to which each substance dissociates as if it were present occupying

<sup>1</sup> In the former paper the words under the curve, *loc. cit.*, p. 1835, "percentage concentration," should read "Grams solute per 100 g. solvent," that being the manner of designating the concentrations in all of the molecular weight determinations in that paper.

a part of the total volume of the solution corresponding to its own mol. fraction of the dissociating substance present; and if we keep in mind the fact that the total amount of dissociating substance in the solutions in the equilibrium experiments was always 30% or more, it appears improbable that any considerable degree of dissociation could have occurred there.

BRYN MAWR, PA.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

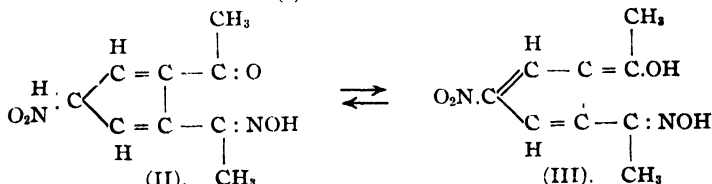
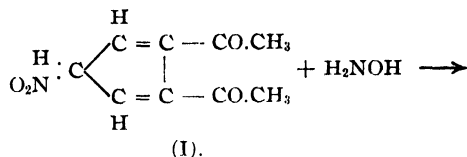
## STUDIES IN THE CYCLOPENTADIENE SERIES. IV. THE FORMATION OF CYCLOPENTADIENODIHYDROPYRIDAZINES.

By WILLIAM J. HALE.

Received September 19, 1916.

In an earlier publication<sup>1</sup> upon 5-nitro-2,3-diacetylcyclopentadiene, attention was called to the fact that only one of the acetyl groups could be involved in the formation of oximes, anils or hydrazones. In a second publication<sup>2</sup> upon 5-nitro-2,3-dibenzoylcyclopentadiene the same general results were experienced. The possibility of steric hindrance interfering with the reaction of hydroxylamine or the hydrazines upon carbonyl groups attached to adjacent carbon atoms presented its usual doubtful significance; its elimination from consideration however followed immediately the study of these monohydrazones.

When, for example, one of the carbonyl groups of diacetylcyclopentadiene (I) enters into reaction there occurs a rearrangement of affinity; a rearrangement from that condition of equilibrium, where either one or the other of these carbonyl groups may exist transitorily in enolic form, to a condition stabilized with reference to one carbonyl group now involved with the basic nitrogen as oxime or hydrazone. The double linking thus established between the nitrogen and the carbon, with the consequent alternate double and single linkings around the ring, leads directly to the enolic form (III) of the second carbonyl group, a form naturally

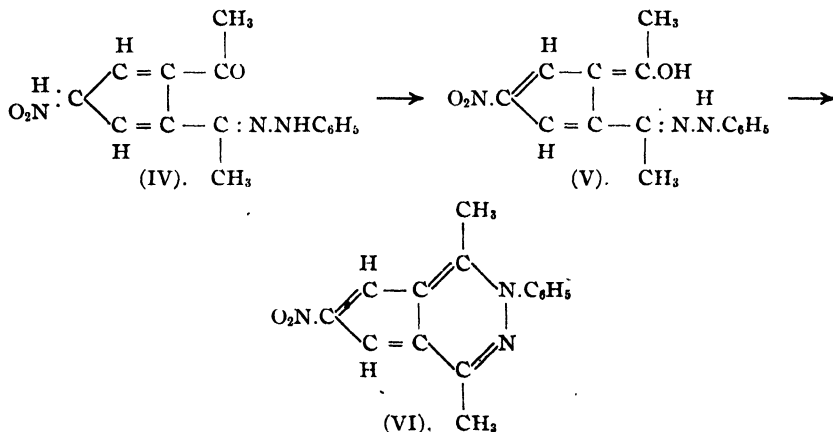


<sup>1</sup> THIS JOURNAL, 34, 1583 (1912).

<sup>2</sup> *Ibid.*, 35, 70 (1913).

in equilibrium with the ketonic form (II) but one now highly favored through this oxime or hydrazone structure. An illustration is afforded by the diagrams on page 2535.

The instability of the monohydrazone and monophenylhydrazones of these cyclopentadiene derivatives has been noted in the earlier publications.<sup>1</sup> In all cases they were found to undergo readily an intramolecular condensation with the production of colored compounds of double ring structure. The study of these compounds has shown that the double ring formation can have proceeded only from the enolic structure shown in (III). When the monophenylhydrazone of 5-nitro-2,3-diacetylcyclopentadiene (IV) is considered, the inner condensation is found to proceed readily from its enolic form (V), even in solutions in anhydrous solvents, to a structure (VI) of the pyridazine type:



This insoluble product, a beautiful orange-yellow in color, is slowly precipitated also from the alkaline solutions of the monophenylhydrazone, the acid hydroxyl and basic hydrogen thus being lost in the production of a neutral pyridazine. This new type of compound must, however, be classed as a cyclopentadienodihydropyridazine.

This development of a pyridazine ring from the 1,2-diacetyl class of compounds at once recalls the history and discussion of the reactions of hydrazine and phenylhydrazine upon diacetosuccinic ester and especially upon acetonylacetone and diphenacyl—the two compounds which were involved in the syntheses of the cyclopentadienes now under consideration. The work of Alexander Smith<sup>2</sup> and of Gabriel and co-workers<sup>3</sup> has established the mode of formation of pyridazines from 1,4-diketones and their derivatives, but in the study of one member of this latter class—

<sup>1</sup> *Loc. cit.*

<sup>2</sup> *Ann.*, **289**, 310 (1896).

<sup>3</sup> *Ber.*, **32**, 395 (1899); **34**, 3257 (1901); **42**, 654 (1909).



diacetosuccinic ester—Curtius<sup>1</sup> procured also a bismethylpyrazolone and later Bülow<sup>2</sup> isolated from this same reaction an N-aminodimethylpyrrole dicarboxylic ester—a compound formed by the simultaneous condensation of one of the amino groups of hydrazine with both of the 1,4-carbonyl groups. This manner of condensation requires the presence of both carbonyl groups in enolic form; it proceeds best in acetic acid solution and to no large yield. According to the structure of diacetylcyclopentadiene, when one of the carbonyl groups reacts in enolic form the second is forced to assume the ketonic structure. It is therefore impossible for a simple pyrrole type of condensation to proceed directly from the cyclopentadiene derivative. Furthermore, all of the products of the condensations for our consideration have failed to show the presence of the pyrrole ring. It is generally accepted also that 5-membered rings when entering into poly-ring nuclei condense more readily with 6-membered rings; hence the possibility of developing a second 5-membered ring—that of a pyrrole—is here disfavored.

Paal and his co-workers<sup>3</sup> observed that diphenacyl, acetylacetone and certain  $\gamma$ -keto esters condensed with hydrazines to form dihydropyridazines; these products were sometimes isolated, but more often were oxidized in the air to the corresponding pyridazines. A similar class of compounds therefore may be expected from the action of hydrazines upon diacetylcyclopentadiene, a compound in which the original stem of these  $\gamma$ -diketones, though now without labile hydrogen, is still present. A few examples of condensed nuclei involving a pyridazine ring as one component have been known. The oxidation of such compounds has unfailingly proved their complete structures. Thus Täuber<sup>4</sup> was the first to prove the structure of phenazone by discovering a pyridazine tetracarboxylic acid in the oxidation product which resulted when phenazone was treated with a very large amount (ten times its weight) of potassium permanganate in neutral solution. Through the loss of two molecules of carbon dioxide from the two carboxyl groups on the two carbon atoms adjacent to the nitrogen atoms there remained finally a 4,5-dicarboxylic acid. Gabriel<sup>5</sup> studied the oxidation of phthalazine by use of potassium permanganate and obtained this same pyridazine dicarboxylic acid as is required by theory. In both of these examples the heterocyclic ring appears the more stable. The oxidation of anisyl cinnoline by Stoermer and Gaus<sup>6</sup> yielded a 4-anisylpyridazine-5,6-dicarboxylic acid, a further indication of the stability of the pyridazine ring. In this latter case,

<sup>1</sup> *J. prakt. Chem.*, [2] 50, 508 (1894).

<sup>2</sup> *Ber.*, 35, 4311 (1902).

<sup>3</sup> *Ibid.*, 36, 491, 497, 2538 (1903); 37, 4382 (1904); 40, 4598 (1907).

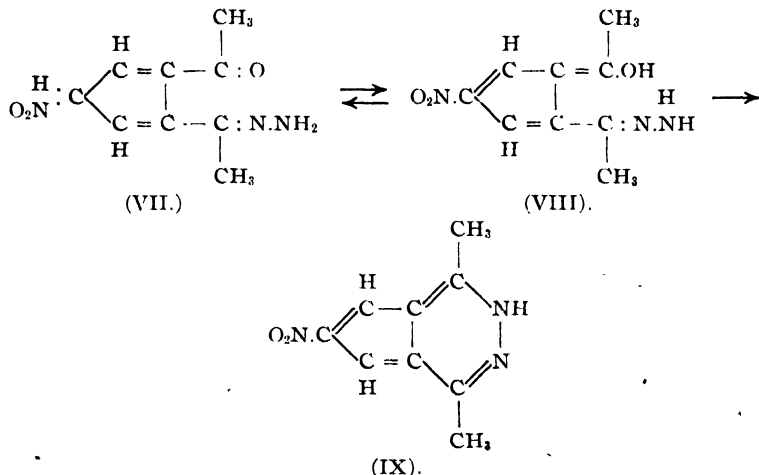
<sup>4</sup> *Ibid.*, 28, 451 (1895).

<sup>5</sup> *Ibid.*, 36, 3373 (1903).

<sup>6</sup> *Ibid.*, 45, 3104 (1911).

as well as in the others, the action of a neutral solution of potassium permanganate at the temperature of the water bath seems most effective for the oxidation of these condensed nuclei to their simple pyridazine derivatives.

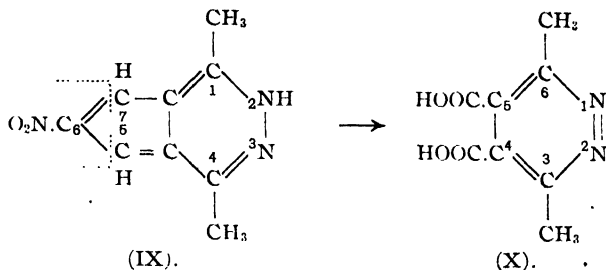
Just as with the monophenylhydrazone of nitrodiacetylcyclopentadiene so also with the monohydrazone (VII) this inner condensation proceeding from its enolic form (VIII) led directly to a cyclopentadienodihydropyridazine (IX) as indicated below:



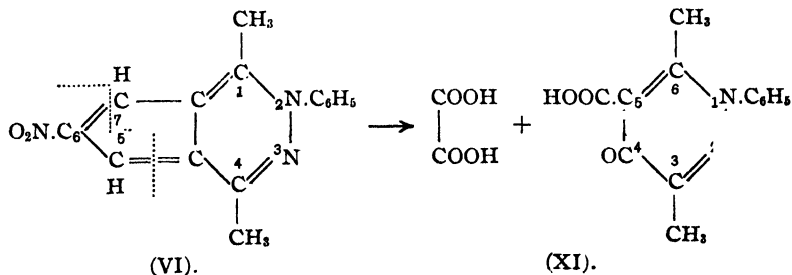
The monohydrazone is very unstable and scarcely can be isolated owing to the great ease with which it undergoes this intramolecular condensation. The absence of any labile hydrogen on a carbon atom adjacent to the second carbonyl group would argue indeed against the appearance of an enolic form in readiness for the further condensation with the hydrazine or phenylhydrazine stem. We may assume, therefore, that the shift in linkings within the cyclopentadiene ring itself, transforming the possible isonitro group to a simple nitro group, is the direct source of this available hydrogen for the second carbonyl group. The replacement of the ketonic oxygen of the first carbonyl group by the basic hydrazine stem acts, of course, as the cause of this directed shift.

A study of the oxidation products of these cyclopentadienodihydropyridazines has led to the following considerations: The orange-red product (IX) obtained from the hydrazone we may term 1,4-dimethyl-6-nitro-2,3-cyclopentadienodihydropyridazine. The diagram on page 2539 will indicate the course of its oxidation by potassium permanganate in neutral aqueous solution. The first break occurs between carbon atoms 6 and 7; the intermediate product—a simple dihydropyridazine derivative—is at once oxidized to the corresponding pyridazine and the second break then occurs between carbon atoms 5 and 6, thus making possible the produc-

tion of two carboxyl groups attached to adjacent carbon atoms in the pyridazine ring. The final product is 3,6-dimethylpyridazine-4,5-dicarboxylic acid (X) a colorless dibasic acid closely resembling the pyridazine dicarboxylic acid already known.

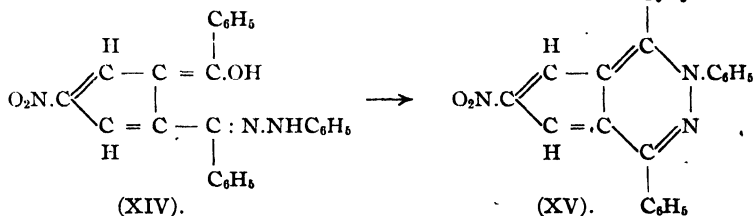
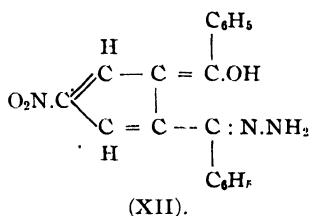


The orange-yellow compound (VI) produced in the intramolecular condensation of the phenylhydrazone of diacetylcyclopentadiene is to be classed as a 2-phenyl-1,4-dimethyl-6-nitro-2,3-cyclopentadienodihydropyridazine. Its oxidation to a dihydropyridazine was best accomplished by the use of potassium permanganate in acetone solution. Its slight solubility in water and alkalies, together with the tendency for an aqueous potassium permanganate solution to carry the oxidation as far as possible toward a pyridazine, required the presence of some solvent which would permit the oxidation to proceed at lower temperatures. In this way the phenyl group upon the nitrogen atom remained in position and the yield of product was not below the ordinary. According to the diagram below the course of the oxidation may be described as a break first occurring between carbon atoms 6 and 7 with the carbon atom 7 passing into carboxyl; the maintenance of the dihydropyridazine structure then forcing the second break between carbon atom 5 and the pyridazine ring. The keto derivative thus formed is a 1-phenyl-3,6-dimethyl-4-ketodihydropyridazine-5-carboxylic acid (XI). This latter is a colorless insoluble monobasic acid. In the mother liquors the presence of nitric and oxalic acids was detected; the latter naturally arises from the elimination of the pair of carbon atoms 5 and 6 in the cyclopentadiene ring. As a check, trial oxidations, where the permanganate had been employed in aqueous



and not in acetone solution, were found to give confirmatory tests for the presence of oxalic acid.

In applying this study to the nitrodibenzoylcyclopentadienes it is found that the monohydrazone (XII) passes most readily into the corresponding 1,4-diphenyl-6-nitro-2,3-cyclopentadienodihydropyridazine (XIII), and that the monophenylhydrazone (XIV) passes almost as quickly into the 1,2,4-triphenyl-6-nitro-2,3-cyclopentadienodihydropyridazine (XV).



The oxidation of these latter products was not attempted. The compounds were beautifully colored and showed all of the reactions characteristic of the former or dimethylpyridazine class.

All of these compounds showed marked stability; their fusion or decomposition points are high and acids or alkalis are practically without action upon them. Their color from a deep yellow to a red is highly characteristic. This stability of the dihydropyridazine ring is of course to be referred directly to the double ring structure; the formation of the stable pyridazine naturally followed wherever possible in the oxidation products. The inner condensation among members of the monoxime class (III) has not yet been studied. It does not, however, proceed with the ease which we should anticipate were there hydrogen directly tied to the nitrogen atom. The condensation therefore must proceed in the manner of anhydrides and require outside agencies which will be considered at another time.

#### Experimental Part.

**1,4-Dimethyl-6-nitro-2,3-cyclopentadieno-1,4-dihydropyridazine**  $\text{C}_7\text{H}_5\text{N}_2(\text{CH}_3)_2(\text{NO}_2)$  (IX).—This compound is best prepared by dissolving 1 g. of 5-nitro-2,3-diacetylcyclopentadiene in 20 cc. of water containing 1 g. of sodium carbonate. To the clear yellow solution is then

slowly added 1 g. of powdered hydrazine sulfate. The yellow monohydrazone which separates in part again redissolves by the heat of the reaction and the orange-red precipitate of the pyridazine shortly makes its appearance. The mixture (which must still be alkaline) is then heated for a few moments over a free flame to insure the solution of any hydrazone or cyclopentadiene unacted upon. Upon filtering the hot mixture the pyridazine is collected upon the filter fairly pure and in excellent yield. This cyclopentadienopyridazine is readily soluble in acetone or acetic ester; fairly soluble in alcohol, acetic acid or benzene; slightly soluble in chloroform, ether or water and insoluble in ligroin. It crystallizes best from alcohol in small beautiful red prisms decomposing at  $240-5^{\circ}$ . As noted in the preparation above this pyridazine is not affected by sodium carbonate. It does, however, dissolve in sodium hydroxide solution to give the sodium salt from which the free substance may again be liberated by acids.

0.1288 g. subst. gave 0.2666 g.  $\text{CO}_2$ , and 0.0570 g.  $\text{H}_2\text{O}$ .

0.1486 g. subst. gave 30.1 cc.  $\text{N}_2$  ( $22.5^{\circ}$  and 738.4 mm. over  $\text{H}_2\text{O}$ ).

Calc. for  $\text{C}_9\text{H}_9\text{O}_2\text{N}_3$ : C, 56.52; H, 4.75; N, 22.00. Found: C, 56.45; H, 4.95; N, 22.12.

**3,6-Dimethyl-4,5-pyridazine Dicarboxylic Acid,  $\text{C}_4\text{N}_2(\text{CH}_3)_2(\text{COOH})_2 \cdot \text{H}_2\text{O}$  (X).**—One gram of the dimethylcyclopentadienodihydropyridazine just described was brought into solution in 100 cc. of water containing just sufficient potassium hydroxide to convert it into the potassium salt. To this clear red solution 5.6 g. of potassium permanganate dissolved in 140 cc. of water (4%) were slowly added and the reaction mixture heated overnight under a reflux condenser at the temperature of the water bath. In the morning a few cc. of the permanganate solution may still be found necessary to complete the oxidation and after a little further heating the excess of permanganate may be decomposed by alcohol and the mixture filtered. The manganese dioxide remaining upon the filter is boiled up once with water and again filtered. The combined filtrates are then acidified with  $\text{HCl}$  and evaporated to dryness upon the water bath. The dry residue is now extracted several times with alcohol and the combined alcoholic extracts evaporated to dryness. This final residue is treated with only a few drops of water (to dissolve salt) and the undissolved portion filtered off. This insoluble portion is then dissolved in hot water, boiled with bone black and filtered; the filtrate, upon evaporation to small volume, yields about 0.2 g. of the colorless dimethylpyridazine dicarboxylic acid. This compound is fairly soluble in alcohol or water; slightly soluble in acetic acid and insoluble in ether, ligroin, chloroform, acetone, acetic ester or benzene. It crystallizes best from water in small colorless prisms decomposing at  $226-8^{\circ}$  and containing one molecule of water of crystallization. In the mother liquors as first obtained in the oxidation described the presence of nitric acid

could just be identified, but besides carbonic acid no other acid was found present. The neutral permanganate solution therefore just sufficed for the splitting off of the one carbon atom out of the cyclopentadiene ring and the conversion of the carbon atoms adjacent to the pyridazine ring into corresponding carboxyl groups as explained previously. The dihydropyridazine, formed in the first step, is of course oxidized immediately to the pyridazine but the methyl groups remain in position unattacked. Had the oxidation not progressed to this stage, tests for the presence of imino hydrogen would have shown other than negative.

0.1676 g. subst. gave 0.2750 g.  $\text{CO}_2$ , and 0.0755 g.  $\text{H}_2\text{O}$ .

0.1436 g. subst. gave 17.6 cc.  $\text{N}_2$  ( $25^\circ$  and 738.9 mm. over  $\text{H}_2\text{O}$ ).

0.1620 g. subst. lost nothing over  $\text{H}_2\text{SO}_4$  but lost 0.0138 g.  $\text{H}_2\text{O}$  at  $112^\circ$ .

Calc. for  $\text{C}_8\text{H}_8\text{O}_4\text{N}_2\cdot\text{H}_2\text{O}$ : C, 44.84; H, 4.71; N, 13.09; 8.42  $\text{H}_2\text{O}$ . Found: C, 44.75; H, 5.04; N, 13.22;  $\text{H}_2\text{O}$ , 8.52.

From this acid a white insoluble silver salt was prepared in the usual manner. Upon analysis

0.1872 g. silver salt gave 0.1304 g.  $\text{AgCl}$ .

Calc. for  $\text{C}_8\text{H}_8\text{O}_4\text{N}_2\text{Ag}_2$ : Ag, 52.64. Found: Ag, 52.43.

A further check on the presence of two carboxyl groups was made by boiling a solution of this acid with Iceland spar contained in a small flask attached to a regular  $\text{CO}_2$  absorption train such as used for combustions. The weight of carbon dioxide liberated is a direct measure of the acid hydrogen.

0.1012 g. subst. liberated 0.0206 g.  $\text{CO}_2$  from  $\text{CaCO}_3$ .

Calc. for  $2\text{H}^+$  in  $\text{C}_8\text{H}_8\text{O}_4\text{N}_2\cdot\text{H}_2\text{O}$ : H, 0.96. Found: H, 0.93.

**2-Phenyl-1,4-dimethyl-6-nitro-2,3-cyclopentadienodihydropyridazine**,  $\text{C}_7\text{H}_2\text{N}_2(\text{C}_6\text{H}_5)(\text{CH}_3)_2(\text{NO}_2)$  (VI).—This product is readily prepared by adding an excess of phenylhydrazine to an alcoholic solution of nitrodiacetylcyclopentadiene (I) and warming the mixture for an hour or more. Upon cooling the precipitation of the pyridazine is practically completed. The isolation of the intermediate monophenylhydrazone is in no wise necessary and rather to be avoided. The yield is almost quantitative. This phenylcyclopentadienopyridazine is readily soluble in chloroform, acetic ester or acetone; it is fairly soluble in alcohol or benzene; slightly soluble in ether or water and insoluble in ligroin. It crystallizes best from alcohol in the form of small yellow needle clusters melting at  $193^\circ$ . It is unaffected by warming with alkali or with acid. In fact the red alkaline solution of the monophenylhydrazone, just mentioned, slowly precipitates this pyridazine in crystalline form.

0.1202 g. subst. gave 0.2962 g.  $\text{CO}_2$  and 0.0552 g.  $\text{H}_2\text{O}$ .

0.1457 g. subst. gave 21.2 cc.  $\text{N}_2$  ( $23.4^\circ$  and 741.4 mm. over  $\text{H}_2\text{O}$ ).

Calc. for  $\text{C}_{15}\text{H}_{15}\text{O}_2\text{N}_3$ : C, 67.39; H, 4.90; N, 15.73. Found: C, 67.22; H, 5.14; N, 15.87.

**1-Phenyl-3,6-dimethyl-4-keto-1,4-dihydro-5-pyridazine Carboxylic Acid**,  $\text{C}_{14}\text{N}_2\text{O}(\text{C}_6\text{H}_5)(\text{CH}_3)_2\text{COOH}$  (XI).—A neutral solution of potassium

permanganate acts very slowly upon the insoluble phenyldimethylcyclopentadienopyridazine. A higher temperature however suffices for a somewhat more rapid oxidation, but is likely also to carry the reaction too far. In order that the phenyl group may remain upon its original nitrogen atom, this oxidation must lead to a dihydropyridazine derivative and hence one may look for a ketodihydropyridazine if the oxidation is successful. This desired result was accomplished through the use of potassium permanganate in acetone solution. One gram of the phenyldimethylcyclopentadienodihydropyridazine in 20 cc. of acetone was slowly added to a solution of 30 g. of potassium permanganate in 600 cc. of acetone, to which previously about 50 cc. of water had been added. The contents of the flask, fitted with reflux condenser, were kept at boiling temperature by means of the water bath. After decolorization of the permanganate still more of this powdered reagent was added little by little until almost another 30 g. were consumed. At this point (after 4 hours' boiling) the decolorization proceeded very slowly and the reaction was considered at an end. The clear filtrate from the reaction mixture was next evaporated to dryness, taken up in a little water, acidified with hydrochloric acid and extracted with ethyl acetate. It is well also to digest the large amount of manganese dioxide with water, filter, evaporate to small volume, acidify and extract with ethyl acetate. From these ethyl acetate extracts the colorless oxidation product is obtained by evaporation. This phenyldimethylketodihydropyridazine carboxylic acid is readily soluble in acetone, chloroform, acetic ester, benzene or acetic acid; it is fairly soluble in alcohol or carbon tetrachloride; slightly soluble in ether or water and insoluble in ligroin. It crystallizes best from alcohol in fine, colorless needles melting at  $220^{\circ}$ .

0.1454 g. subst. gave 0.3414 g.  $\text{CO}_2$  and 0.0674 g.  $\text{H}_2\text{O}$ .

0.1359 g. subst. gave 14.6 cc.  $\text{N}_2$  ( $22^{\circ}$  and 735.4 mm. over  $\text{H}_2\text{O}$ ).

Calc. for  $\text{C}_{18}\text{H}_{12}\text{O}_3\text{N}_2$ : C, 63.90; H, 4.96; N, 11.43. Found: C, 64.04; H, 5.18; N, 11.71.

As this acid does not form an insoluble silver salt or similar product adapted to a simple analysis the presence of the single carboxyl group was determined from the weight of carbon dioxide liberated when the acid, a little water and some alcohol, to aid its solution, were brought in contact with barium carbonate in a small flask as described in a previous experiment.

0.1346 g. subst. liberated 0.0118 g.  $\text{CO}_2$  from  $\text{BaCO}_3$ .

Calc. for  $1\text{H}^+$  in  $\text{C}_{18}\text{H}_{12}\text{O}_3\text{N}_2$ : H, 0.41. Found: H, 0.40.

The barium carbonate worked to a better advantage in this case than the iceland spar.

The production of this ketodihydropyridazine carboxylic acid leaves no room for doubt concerning the original structure of the double ring molecule. The oxidation must have proceeded as indicated, (VI) into

(XI), and oxalic acid should be found as a by-product. Both the liquors, from the oxidation at lower temperatures in acetone solution and the trial oxidation carried out in neutral aqueous solution at the temperature of the water bath, gave distinct and positive tests for the presence of oxalic acid. Nitric acid also was present in traces.

**1,4-Diphenyl-6-nitro-2,3-cyclopentadienodihydropyridazine**,  $C_7H_3N_2 \cdot (C_6H_5)_2(NO_2)$  (XIII).—This product is prepared by dissolving nitrodibenzoylcyclopentadiene<sup>1</sup> in a mixture of benzene and alcohol and adding an excess of hydrazine hydrate in alcoholic solution. The clear red solution is then warmed on a water bath for a few hours when the precipitation of the diphenylcyclopentadienopyridazine will be found complete. This substance is only fairly soluble in acetone, acetic ester, chloroform, benzene, alcohol or acetic acid; it is slightly soluble in ether and insoluble in ligroin or water. It crystallizes best from acetone in small orange-red prisms decomposing at  $275-80^\circ$ . This diphenyl derivative is not affected by acids or dilute alkalies; it is, however, soluble in alcoholic sodium hydroxide and may again be precipitated from this solution by acid. No successful means presented itself for the isolation of the intermediate monohydrazone (XII) owing to its great instability.

0.1376 g. subst. gave 0.3658 g.  $CO_2$  and 0.0562 g.  $H_2O$ .

0.1470 g. subst. gave 18.3 cc.  $N_2$  ( $24.2^\circ$  and 738.6 mm. over  $H_2O$ ).

Calc. for  $C_{18}H_{13}O_2N_3$ : C, 72.36; H, 4.16; N, 13.34. Found: C, 72.52; H, 4.57; N, 13.48.

**1,2,4-Triphenyl-6-nitro-2,3-cyclopentadienodihydropyridazine**,  $C_7H_2N_2 \cdot (C_6H_5)_3(NO_2)$  (XV).—This is prepared by digesting a hot benzene solution of nitrodibenzoylcyclopentadiene with an excess of phenylhydrazine for 8 or 9 hours at the temperature of the water bath. The red crystals of the triphenyl derivative are slowly precipitated. The monophenyl hydrazone as described by Thorp and the writer<sup>2</sup> might first have been prepared and its conversion to the pyridazine accomplished simply by boiling its solution in alcohol or benzene; this step, however, is unnecessary and not to be recommended. Triphenylcyclopentadienopyridazine is only fairly soluble in chloroform or benzene; slightly soluble in acetone, acetic ester or acetic acid and insoluble in ether, alcohol, ligroin or water. It crystallizes best from chloroform in small orange-red prisms melting sharply at  $287^\circ$ . It is unaffected by acids and alkalies.

0.1710 g. subst. gave 0.4823 g.  $CO_2$  and 0.0734 g.  $H_2O$ .

0.1850 g. subst. gave 19.1 cc.  $N_2$  ( $25^\circ$  and 718 mm. over  $H_2O$ ).

Calc. for  $C_{28}H_{17}O_2N_3$ : C, 76.70; H, 4.38; N, 10.74. Found: C, 76.93; H, 4.81; N, 10.81.

The formation of this new class of compounds, the condensed 5-carbon ring and pyridazine, is made possible through the presence of a basic hydrogen atom in the hydrazine substituent of the carbocyclic ring in

<sup>1</sup> *Loc. cit.*

<sup>2</sup> THIS JOURNAL, 35, 73 (1913).



proper position to an hydroxyl in an adjacent substituent. For the aid granted by the trustees of the Wolcott Gibbs Fund in the prosecution of this research and for the assistance rendered on this account by Messrs. G. O. Gutekunst and Edgar C. Britton the writer wishes to express his appreciation and indebtedness.

ANN ARBOR, MICH.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRESIDENCY COLLEGE.]

## HALOGENATION. XIV. BROMINATION OF HYDROCARBONS BY MEANS OF BROMINE AND NITRIC ACID.

BY RASIK LAL DATTA AND NIHAR RANJAN CHATTERJEE.

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In continuation of the researches of the action of *aqua regia* on organic bodies in general, the study of the action of a mixture of nitric and hydrobromic acids was taken in hand. In analogy with the action of *aqua regia*, it was thought that a mixture of nitric and hydrobromic acids, which is capable of giving bromine in the nascent state, would effect brominations more satisfactorily than bromine, and this has been found to be the case. The bromination of benzene has been effected by this reagent with the formation of monobromobenzene in good yield. As a considerable amount of nitric acid is used up, in the first instance, to liberate bromine from hydrobromic acid, it was found satisfactory to employ bromine and nitric acid only. In fact, the mixture of the acids is less active than bromine and nitric acid on account of the water added as the medium of hydrobromic acid.

As bromination could as well be carried out directly with or without the help of a carrier, the advantages of the method may be pointed out. In the case of ordinary bromination with or without carrier, the reaction is one of substitution, liberating an amount of hydrobromic acid equal to that of bromine which enters the molecule. But in the case of bromination in the presence of nitric acid, all the bromine enters the molecule, the nitric acid helping the oxidation of hydrobromic acid to bromine, as soon as it is formed. This bromine is available for further bromination. Hence it is evident that only half the usual amount of bromine will be required for brominations by this method. Here the nitric acid acts as the oxidizing agent facilitating the introduction of bromine, itself being reduced to nitrous gases. Furthermore, the reagent is very active, effecting brominations very rapidly and energetically, so much so that frequent rupture of substances subjected to its action is the result. Those brominations which require a considerable time for their course even with the help of a carrier, could be effected most speedily and satisfactorily. The method is specially suitable for tolerably light hydrocarbons but with the higher ones the process is not quite satisfactory as the chances of

nitration are also great on account of the strong nitric acid, as has been pointed out before in the course of chlorination by means of *aqua regia*.<sup>1</sup> In fact, the chances of bromination are greater in the lower hydrocarbons whereas, in the cases of higher hydrocarbons the chances of nitration are greater. These also depend upon the specific nature of the compounds.

As has already been pointed out, a mixture of bromine and nitric acid has been found to be quite a satisfactory brominating agent, giving bromo-derivatives with the aromatic hydrocarbons, the proportion of any particular bromo-derivative depending upon the duration of the reaction. It will be shown later that the reagent is very active and has a simultaneous brominating and oxidizing action with the formation of tetrabromoquinone as end product of such actions. With other organic compounds, aliphatic or aromatic, which break up under the influence of this reagent, bromopicrin seems to have been generally produced.

The results obtained in the bromination of hydrocarbons by this reagent are interesting. Benzene gives a good yield of bromobenzene by carrying on the process for a short time. If, however, the process be prolonged for some time, *p*-dibromobenzene is the chief product. Toluene gives *o*-bromotoluene and 3,4-dibromotoluene on short action while pentabromotoluene is formed by the prolonged action of the reagent. *o*-Xylene yields monobromo-*o*-xylene readily, while tetrabromo-xylene is the main product of a prolonged action. In the latter case, the product is accompanied by small quantities of *p*-toluic and *o*-toluic acids due to the prolonged oxidizing influence of nitric acid. From *m*-xylene, monobromo-*m*-xylene as also dibromo-*m*-xylene have been obtained on acting with the reagent for a short time, while tetrabromo-*m*-xylene is the product of a somewhat prolonged action. *p*-Xylene gives monobromo-*p*-xylene and dibromo-*p*-xylene, while the prolonged action produces tetrabromo-*p*-xylene. Mesitylene forms monobromo-mesitylene in the cold, while tribromo-mesitylene is the chief product upon heating. With ethyl benzene, monobromo-ethyl benzene is the chief product, but on prolonged action a complicated product is formed which could not be separated and purified.

#### Mixture of Hydrobromic and Nitric Acid as a Brominating Reagent.

**Bromination of Benzene.**—Benzene could be brominated readily by a mixture of hydrobromic and nitric acids with the formation of bromobenzene.

Equal volumes of hydrobromic acid (47%) and nitric acid (sp. gr. 1.35) were gradually mixed in a flask fitted with a reflux condenser and to this benzene is added equal to a fourth part of the acid mixture. The heavy layer of nitrosyl tribromide<sup>2</sup> settles at the bottom while the benzene

<sup>1</sup> THIS JOURNAL, 36, 1007 (1914).

<sup>2</sup> The detailed description of this substance will be communicated shortly.

floats at the top. The reaction is then started by placing the flask on the water bath, removing it from time to time when the vigor of the reaction becomes uncontrollable, which is evident from the escape of considerable amounts of bromine. All the time during the course of the reaction a steady evolution of nitrous fumes takes place. When the evolution of nitrous fumes has ceased the reaction becomes complete. A heavy brown oil is seen deposited at the bottom of the aqueous layer. This is washed with dilute alkali, dried and then distilled. Unchanged benzene comes over at  $80^{\circ}$ , then the temperature rises gradually and most of the product comes over between  $153\text{--}154^{\circ}$  which is the boiling point of bromobenzene. The fraction was again redistilled and the identity was established by a bromine estimation.

Calc., Br = 50.95. Found, Br = 50.35.

The yield obtained by this method is quite satisfactory amounting to 80% of the theory.

#### Bromination by Means of Bromine and Nitric Acid.

**Benzene.**—When the bromination is carried out with the calculated quantities of bromine and nitric acid for a comparatively short time, bromobenzene is the chief product, whereas, if the bromination be carried on with an excess of bromine and nitric acid for a good length of time, *p*-dibromobenzene is the chief product. Other higher bromo-derivatives of benzene could not be obtained, however long the action is carried out. For the preparation of monobromobenzene 36 cc. of benzene are taken in a flask fitted with a reflux condenser and to this 10 cc. of conc. nitric acid and 10.7 cc. (32 g.) of bromine are gradually added. The reaction does not seem to take place at the ordinary temperature. The flask is then placed on the water bath when the reaction begins to take place, as is evident from a steady evolution of brown fumes of oxides of nitrogen. The operation is continued for five hours with the further addition of a little more nitric acid. The mixture refluxes only slightly at the end due to the conservation of benzene into bromobenzene. The heavy oily layer underneath the aqueous layer is taken out, washed with dilute alkali and then dried by means of calcium chloride. It is next distilled over wire gauze in a flask provided with a two-bulbed still-head. Unchanged benzene comes over at about  $80^{\circ}$ , then the temperature rises to about  $140^{\circ}$  when the receiver is changed and bromobenzene is collected until the temperature rises to  $170^{\circ}$ . A dark, viscous residue is left behind within the flask weighing about 2–3 g., which is a mixture of the higher bromo-derivatives. The fraction  $140\text{--}170^{\circ}$  is redistilled and is found to boil at  $153\text{--}154^{\circ}$ . The yield obtained is 60% of the theory. To establish the complete identity of the substance, bromine in the sample was estimated.

Calc., Br = 50.95. Found, Br = 50.47.

It was thought that by using fuming nitric acid, the course of the reaction could be shortened a good deal, but in practice it was not possible. On the other hand, fuming nitric acid diminished the yield on account of its great hydrolyzing action.

For the preparation of *p*-dibromobenzene, 8 g. of benzene are taken in a flask with 12 g. of bromine and 3 cc. of nitric acid. The mixture is at the first instance warmed on the water bath for six hours, when it is found that the mixture refluxes no more, due to the formation of bromobenzene. Then 12 g. more of bromine are added with 3 cc. of nitric acid and the mixture is heated on a sand bath for six hours more when the operation is found to be complete. The semisolid product is separated from the layer of water and heated in a basin to drive off unchanged benzene and bromine, when, on cooling, it begins to solidify and the solidification is hastened by stirring with a glass rod. The crystals were next pressed between the folds of a blotting paper and then recrystallized from alcohol, when *p*-dibromobenzene is obtained in beautiful plates melting at 87°. The yield obtained is nearly quantitative.

Calc., Br = 67.80. Found, Br = 67.45.

**Toluene.**—Toluene gives a mixture of *o*-bromotoluene and 3,4-dibromotoluene by carrying the reaction for a very short time, while by carrying on the reaction for a rather long time with an excess of bromine and nitric acid, penta-bromotoluene is the chief product.

For the preparation of *o*-bromo- and dibromotoluene, 10 cc. of toluene are taken in a flask fitted with a reflux condenser and to this 4 cc. of nitric acid (sp. gr. 1.35) are added and to the mixture 6 cc. of bromine are gradually added in small portions at a time. The reaction takes place almost immediately the substances are mixed, and fumes of oxides of nitrogen are evolved. After a short time, the reaction subsides and nitrous fumes cease to evolve. The mixture is further warmed on the sand bath for half an hour more, when the reaction seems to proceed again with the evolution of nitrous fumes and at the end no more of it comes out, proving that the reaction is complete. The deep brown oil formed is next treated with dilute alkali, washed and dried by means of fused calcium chloride. The dried oil is next distilled. No unchanged toluene comes over; the first fraction was collected between 180–190° and the second fraction, between 200–250°. In the distilling flask there remained behind a charred liquid which consists of higher bromo-derivatives of toluene. On redistilling the first fraction 4 cc. (5.3 g.) of *o*-bromotoluene is obtained, boiling at 180°, while from the second fraction 1 cc. of 3,4-dibromotoluene, boiling at 240–241° has been isolated. Yield of *o*-bromotoluene is 40% of the theory.

For the production of pentabromotoluene the following details are carried out: 5 cc. of toluene are taken in a flask fitted with a condenser

and to this 2 cc. of nitric acid are added from a pipet and then bromine is added gradually in the course of the reaction in 2 cc. at a time. The mixture is warmed on the sand bath, slowly at first, but gradually increasing the temperature of the bath, when it is found that the heavy liquid formed does not reflux so easily. Bromine and a little nitric acid are added from time to time as they are used up. The operation takes about three hours to complete. A dark brown, pasty product is obtained which is chiefly pentabromotoluene mixed with small quantities of the lower bromo-derivatives. For their separation, steam distillation has been found to be very effective. The lower bromo-derivatives come over with the steam, leaving behind a light yellow crystalline product, which is practically pure pentabromotoluene. The crystals were next washed with ether to free them from adhering impurities in which they are insoluble, giving pure pentabromotoluene. This is sublimed and the sublimed product is found to melt at  $280^{\circ}$ . The yield obtained is nearly quantitative.

Calc., Br = 82.13. Found, Br = 81.66.

In the case of toluene, a sweet smell is noticed during the progress of the reaction, which is especially noticeable when purifying the products. This sweet smelling vapor attacks the eyes most powerfully, causing an abundance of tears and considerable amount of pain. This is due to the formation of a small quantity of benzyl bromide.

***o*-Xylene.**—This yields monobromo-*o*-xylene by the short action of bromine and nitric acid, while by the prolonged action, tetrabromo-*o*-xylene is obtained accompanied by *o*- and *p*-toluic acids. For the preparation of monobromo-*o*-xylene, 10 cc. of *o*-xylene are taken in a flask provided with a reflux condenser and to this about 5 cc. of strong nitric acid and 8 g. of bromine are added. The reaction at once starts in with the evolution of brown fumes. After the reaction has subsided the material is warmed on the sand bath for about half an hour, when the operation is found to be complete. The oil is washed, dried and distilled. At first a little unchanged *o*-xylene comes out, then the temperature rises rapidly to  $210^{\circ}$  and the liquid distilling between  $210$ – $220^{\circ}$  is collected separately. After a second distillation it is found to consist of pure monobromo-*o*-xylene boiling at  $214$ – $215^{\circ}$ , the yield obtained being 6 cc. (8.22 g.) or 60% of the theory.

Calc., Br = 43.24. Found, Br = 42.95.

The prolonged bromination of *o*-xylene is carried out as follows: 4 cc. of *o*-xylene are taken in a flask provided with a ground reflux condenser and to this about 2 cc. of strong nitric acid are added and bromine in considerable excess in small quantities from time to time. The whole mixture is heated on the sand bath for about ten hours, when a semisolid product is obtained. The semisolid mass is warmed on the water bath

to free it from unchanged bromine. A brown oily substance is left behind, which is boiled with distilled water. The aqueous extract is decanted off and is allowed to evaporate on the water bath, when a white crystalline substance is obtained, which is found on examination to be *p*-toluic acid melting at  $180^{\circ}$ . The yellow oil obtained in the above operation is found to crystallize when kept aside for a day or two. It is next extracted by means of alcohol, when a part dissolves and gives crystals on evaporation which has been found to melt at  $101^{\circ}$  and on examination is found to be *o*-toluic acid.

The white crystalline substance remaining after alcoholic extraction is found to consist of impure tetrabromo-*o*-xylene, which could, however, be purified with difficulty. It melts between  $250^{\circ}$  and  $256^{\circ}$ .

Calc., Br = 75.82. Found, Br = 75.22.

*m*-Xylene forms a mixture of monobromoxylene and dibromoxylene by the action of bromine and nitric acid, but the product is tetrabromoxylene if the reaction be prolonged for a considerable time. For the preparation of monobromoxylene and dibromoxylene, 10 cc. of *m*-xylene are mixed with 5 cc. of strong nitric acid and 15 g. of bromine, when the reaction starts itself in the cold. After the first action has subsided the reaction mixture is warmed on the water bath for about two hours. The heavy oil that is found to have formed in the reaction is next washed, dried and distilled. Practically no unchanged xylene comes over. The distillate is collected in two fractions, one between  $200-210^{\circ}$  and the other between  $245-260^{\circ}$ . The first portion consists mainly of monobromo-*m*-xylene and the second portion contains dibromo-*m*-xylene. The first fraction is redistilled and found to boil at  $205^{\circ}$ . The yield of the monobromo-derivative obtained is 4 g.

Calc., Br = 43.24. Found, Br = 42.67.

The second fraction solidifies completely after allowing it to stand for some time. The crystals are pressed to free it from adhering liquor and then recrystallized and it is found to melt at  $68^{\circ}$ , the yield obtained being 4.5 g.

Calc., Br = 66.60. Found, Br = 60.27.

For the preparation of tetrabromoxylene 12 cc. of *m*-xylene are heated in the above manner with 4 cc. of nitric acid and an excess of bromine. The mixture is heated on the sand bath for ten hours, bromine being added in small quantities at a time. Occasional replenishing of nitric acid is also necessary. At the end of the operation a semisolid brown mass is obtained. It is first warmed on the water bath to drive off any free bromine present in it. The mass is boiled with water and on cooling the aqueous extract yields beautiful, white silky crystals. The crystals thus obtained are found to be pure tetrabromo-*m*-xylene, melting at  $241^{\circ}$ . The yield obtained is 6 g.

Calc., Br = 75.82. Found, Br = 75.34.

It is necessary to point out that the crystals obtained as the result of first solution in hot water consists of pure tetrabromo-xylene, while the product from subsequent washings contain impurities in the shape of lower bromo-derivatives. The yellow, viscous liquid consists of lower bromoxylenes amounting to 2.4 g. This can be separated, by the method given before, into monobromo- and dibromoxylenes.

***p*-Xylene.**—Eight cc. of *p*-xylene are taken in a flask with 2 cc. of conc. nitric acid and 2 cc. of bromine. Within a short time the reaction begins and nitrous fumes are seen to evolve. After warming on sand bath for fifteen or twenty minutes, the reaction is found to be complete. The oil is next washed, dried and distilled. At first only a small quantity of unchanged xylene comes over between 130–140°. Then the thermometer rises rapidly and monobromo-*p*-xylene distills over between 195–205°, the next fraction distilling between 255–265°, which consists of dibromo-derivative. The first fraction is redistilled and is found to boil at 199–200°. The yield obtained is 5 cc. (6.96 g.), *i. e.*, 55% of the theory.

Calc., Br = 43.24. Found, Br = 42.83.

The second fraction is purified by freezing, on placing it in a mixture of ice and salt. The crystals are pressed out from the adhering impurities. It melts at 75° and is found to be pure 2,5(s)dibromo-*p*-xylene. The yield obtained being 2 cc.

Calc., Br = 60.60. Found, Br = 60.12.

For the preparation of the higher bromo-derivatives of *p*-xylene, 4 cc. of *p*-xylene are heated on a sand bath for about twelve hours with nitric acid and bromine; the latter is added in small quantities from time to time. At the end a semisolid product is obtained which is freed from unchanged bromine by heating on water bath. The solid mass consists of a mixture of *p*-toluic acid and tetrabromo-*p*-xylene. A partial separation can be effected by treatment with alcohol but a complete separation to obtain pure products was not found successful.

**Mesitylene.**—Seven and five-tenths cc. of mesitylene are taken in a flask with a ground condenser and to it 2 cc. of nitric acid and 2 cc. of bromine are added. Reaction at once sets in and it is completed by warming for a few minutes on the sand bath. The heavy oil which is formed as a product of the reaction is washed, dried and distilled. It contains practically no unchanged mesitylene, the greater part is monobromo-mesitylene and comes over between 230–233°. The yield obtained is 4 g., or 46% of the theory.

Calc., Br = 40.21. Found, Br = 39.98.

A tarry residue is left behind in the flask which is a mixture of the higher bromo-derivatives.

By the prolonged action of bromine and nitric acid on mesitylene, tribromo-mesitylene is the chief product.

7.5 cc. of mesitylene are treated with 3 cc. of nitric acid and 6 cc. of bromine. The reaction starts at once and it is continued on a sand bath for three hours; bromine and nitric acid are added gradually in small portions at a time. A semisolid mass is obtained which is warmed on a basin with water to drive off the volatile matter. The product solidifies on cooling and consists of practically pure tribromo-mesitylene. The product on washing with benzene leaves behind white, silky crystals which are found to be pure tribromo-mesitylene, melting at  $222-223^{\circ}$ . The yield obtained is 5.5 g. of tribromo-mesitylene, or 33% of the theory.

Calc., Br = 67.22. Found, Br = 66.83.

**Ethyl Benzene.**—Ethyl benzene gives on short bromination with bromine and nitric acid, a mixture of *o*- and *p*-bromoethyl-benzene. For its preparation, 7 cc. of ethyl benzene are treated with 3 cc. of nitric acid and 4 cc. of bromine. The reaction begins at once with the evolution of nitrous fumes and generally the reaction becomes complete even without warming. The resulting product is washed, dried and distilled. After the passing out of unchanged ethyl benzene, the greater part boiled between  $202-204^{\circ}$ , which is a mixture of *o*-bromoethyl-benzene and *p*-bromoethyl-benzene. The yield obtained is 6 g., or 55% of theory.

Calc., Br = 43.24. Found, Br = 42.11.

After the distillation, a charred residue is left behind in the flask which is a mixture of higher bromo-derivatives of ethyl benzene.

Investigations on similar lines are being continued.

CHEMICAL LABORATORY, PRESIDENCY COLLEGE,  
CALCUTTA.

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[CONTRIBUTION FROM THE EXPLOSIVES LABORATORY OF THE BUREAU OF MINES, DEPARTMENT OF THE INTERIOR.]

## APPLICATION OF THE NITROMETER FOR THE DETERMINATION OF CONSTITUTION AND ESTIMATION OF NITROGEN IN A CLASS OF NITROCOMPOUNDS. (NITROAMINES.)<sup>1</sup>

BY W. C. COPE AND J. BARAB.

Received September 21, 1916.

The nitrometer reaction was first noted by Crum<sup>2</sup> in 1847; but it was not until 1878 when Lunge<sup>3</sup> succeeded in developing a practical instrument which he called the "nitrometer" that this reaction came into general use. Undoubtedly the most common application of the nitrometer is for

<sup>1</sup> Published by permission of Director, Bureau of Mines.

<sup>2</sup> *Phil. Mag.*, [3] 30, 426 (1847).

<sup>3</sup> *Ber.*, 11, 436; *Chem. News* 38, 18 (1878); *Dingler's Polytech. J.*, 228, 448 (1878).



the estimation of nitrogen as nitric oxide (NO) in nitric and nitrous acids their salts and esters. However, the nitrometer is by no means limited to these reactions.

In the literature may be found applications of the nitrometer for analyses of a great variety of compounds. According to Lunge<sup>1</sup> it may be employed in general for all analytical operations in which a definite quantity of gas is evolved, not soluble to a very considerable extent in the liquid from which it is evolved, and not acting upon mercury. He employs the nitrometer for determining the strength of standard acids, by introducing into the nitrometer a measured volume of the acid with an excess of sodium or calcium carbonate and measuring the volume of CO<sub>2</sub> liberated. From this the strength of the acid may be calculated. By using a weighed quantity of carbonate and an excess of acid the carbonate may be determined. The strength of hydrogen peroxide may be determined by measuring the volume of oxygen evolved by the action of bleaching powder and *vice versa*. Potassium ferricyanide in alkaline solution liberates oxygen from hydrogen peroxide and may be analyzed in like manner. Lunge also employed the nitrometer for estimating indigotin in reducing solutions of indigo, by means of absorption of oxygen. For a further list of methods and of the varied application of the nitrometer, Warrington,<sup>2</sup> Allen<sup>3</sup> and Baumann<sup>4</sup> should be consulted.

The fact that in the nitrometer it is possible to obtain the nitrogen as NO from nitric and nitrous esters and not from most characteristic nitrocompounds has long been used as a means of distinguishing the respective esters from nitrocompounds. A statement to this effect was made by Lunge<sup>5</sup> as follows:

"I have also made experiments to determine whether characteristic nitrocompounds will liberate nitric oxide as do the nitric esters by shaking with sulfuric acid and mercury. Although not apparent it would not seem impossible, that under these conditions sulfonic acids form and the feed nitric acid would react upon mercury, *e. g.*,  $C_6H_5NO_2 + SO_3H_2 = C_6H_5SO_3H + NO_2H$ . But nitrobenzol with sulfuric acid on the most vigorous shaking in the nitrometer gave no trace of gas, and furthermore remained unchanged. One may, therefore, safely conclude that the characteristic nitrocompounds have this distinction from the nitric esters of glycerin, cellulose, and other analogous compounds."

As further evidence of the stability of characteristic compounds toward the nitrometer reaction the following nitrocompounds were investigated in this laboratory: Nitromethane, CH<sub>3</sub>.NO<sub>2</sub>; dinitrobenzene, *o*-, *m*- and *p*-C<sub>6</sub>H<sub>4</sub> : (NO<sub>2</sub>)<sub>2</sub>; dinitrophenol, 1 : 2 : 4, C<sub>6</sub>H<sub>3</sub>(OH) : (NO<sub>2</sub>)<sub>2</sub>; dinitronaphthalene, 1 : 8, C<sub>10</sub>H<sub>6</sub> : (NO<sub>2</sub>)<sub>2</sub>; trinitrotoluene, 1 : 2 : 4 : 6,

<sup>1</sup> *J. Soc. Chem. Ind.*, 4, 447 (1885).

<sup>2</sup> *J. Chem. Soc.*, 35, 375 (1879).

<sup>3</sup> *J. Soc. Chem. Ind.*, 4, 178 (1885).

<sup>4</sup> *Z. angew. Chem.*, 4, 135, 203, 328, 339, 392, 450 (1891).

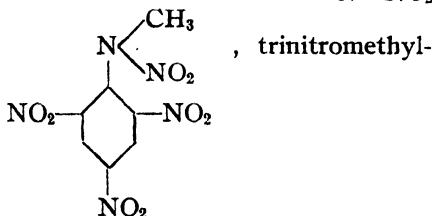
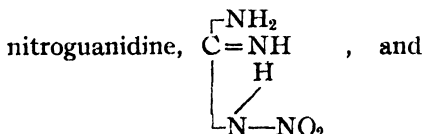
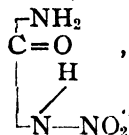
<sup>5</sup> *Dingler's Polytechnic. J.*, 245, 171 (1882).

$C_6H_2(CH_3) : (NO_2)_3$ ; and tetranitroaniline, 1 : 2 : 3 : 4 : 6,  $C_6H_4(NH_2) : (NO_2)_4$ .

In no case with any of the above nitrocompounds could any gas be detected in the nitrometer on the most vigorous shaking with sulfuric acid and mercury. In all the above compounds it should be noted that the nitrogen of the nitro group is attached directly to the carbon atom.

In summarizing other reactions which identify characteristic nitrocompounds and nitrous and nitric esters we find the lines rather sharply drawn. The esters are more or less readily saponified by caustic potash into alcohols and the respective salts. Nitrocompounds are not saponifiable. When caustic potash reacts upon these, the products of reaction are not alcohols and nitrites or nitrates. By reduction the esters are converted into alcohol and ammonia, while the nitrocompounds under similar conditions yield as final products aminocompounds. The acid character of the aliphatic nitrocompounds is shown by the fact that one hydrogen atom attached to the same carbon atom as the nitro group is readily replaced by a metal. This cannot apply to the aromatic compounds, since the nitro group is attached to a tertiary carbon atom.

We will now turn to a class of nitrocompounds, the nitroamines, in which the nitro group is attached to carbon through nitrogen. As examples of this class of compounds we will cite nitrourea,



nitramine, usually called tetranitromethylaniline and known commercially as "tetryl."

In spite of the strongly basic character of guanidine, nitroguanidine<sup>1</sup> is a feebly acid substance. When boiled with caustic potash,  $CO_2$ ,  $N_2O$  and ammonia are formed. With zinc dust and acetic acid nitrosoguanidine and then aminoguanidine are formed. By treating with a hydrochloric acid solution of stannous chloride, ammonia and guanidine are formed.

Nitro urea is a strong acid;<sup>2</sup> its alkali salts are neutral in reaction and it expels acetic acid from acetates. From this reaction it should be con-

<sup>1</sup> Beilstein, Vol. I, 1163.

<sup>2</sup> Richter's "Organic Chemistry" (Spielman), I, p. 441.

$$\begin{array}{c}
 \text{N}=\text{N}=\text{O} \\
 \quad \quad \quad \diagdown \\
 \quad \quad \quad \text{OH} \\
 | \\
 \text{C}=\text{O} \\
 | \\
 \text{NH}_2
 \end{array}$$
 sidered an iso-nitrocompound, . On reduction it gives first nitroso and then aminourea.

Trinitromethylnitramine undoubtedly also gives all the characteristic reactions of true nitrocompounds. This compound is of particular interest because it has three nitro groups attached directly to the carbons in the ring and one nitro group linked to carbon through a secondary nitrogen.

The nitroamines described were selected at random as types of nitrocompounds in which the nitro group is attached to carbon through nitrogen. The reactions indicated show them to respond to most reactions for true nitrocompounds. When subjected to the nitrometer reaction they yielded only the nitrogen of the nitro group attached to carbon through nitrogen. In this reaction they behave like the nitric and nitrous esters.

The du Pont<sup>1</sup> modification of the Lunge nitrometer and the decomposition flask method of Berl and Jurrissen<sup>2</sup> were used in the determination of nitrogen. The decomposition flask method of Berl and Jurrissen is not known generally in this country and, therefore, a short description of the apparatus and method of operation will be appropriate. The apparatus consists of a heavy-walled round-bottom flask of 300 cc. capacity, with a ground-in bulb-shaped glass fitting. The fitting is composed of two parts: a 50 cc. tap funnel through the side of the bulb, with its stem extending below the neck of the flask; and an exit tube, containing a two-way stop-cock, in the top of the bulb. The fittings and cocks are all greased with a mixture of vaseline and caoutchouc.

The substance to be analyzed is placed in the flask, which is then closed with the fitting. The flask is evacuated through the exit tube and CO<sub>2</sub> introduced. This operation is repeated three times and the flask is finally again exhausted. About 20 cc. conc. H<sub>2</sub>SO<sub>4</sub> are added through the tap funnel, and the flask is shaken until the substance dissolves. Ten to fifteen grams of mercury are then added through the funnel and the flask shaken until NO is completely evolved.

The success of this method depends principally upon good fittings and pure CO<sub>2</sub>. By using a CO<sub>2</sub> generator similar to the one described by Young and Caudwell<sup>3</sup> and developed by one of us<sup>4</sup> in this laboratory, no difficulty was experienced in obtaining a supply of pure CO<sub>2</sub>. The gas generated in the flask is displaced by the rapid introduction of a saturated solution

<sup>1</sup> *J. Soc. Chem. Ind.*, 19, 982 (1900).

<sup>2</sup> *Z. angew. Chem.*, 23, 241 (1910).

<sup>3</sup> *J. Soc. Chem. Ind.*, 26, 184 (1907).

<sup>4</sup> "Determination of Nitrogen in Substances Used in Explosives," Bur. Mines, *Tech. Paper* 160.

of sodium sulfate through the funnel and is collected in a buret over mercury. The volume is observed, the gas run into a caustic potash solution, returned to the buret and the reading taken. The quantity of  $\text{CO}_2$  absorbed varies from two to three cubic centimeters. The gas is then passed into a pipet containing a saturated solution of ferrous sulfate and well shaken. The residual gas is then returned to the buret and the reading observed. The residual gas varies from 1.5 to 2.0 cc. In treating a sample of gas obtained in the nitrometer from  $\text{KNO}_3$  in above manner it was found that a 100 cc. sample left a residue of 1.7 cc. It was consequently considered permissible to add this residual gas to the  $\text{NO}$  absorbed by ferrous sulfate. From this volume, after reducing to standard conditions, the percentage of nitrogen was calculated.

Representative samples of gas from each of the compounds analyzed in the du Pont nitrometer were passed into  $\text{FeSO}_4$  solution and in all cases gave results that left no doubt that the gas consisted entirely of nitric oxide.

TABLE OF NITROGEN DETERMINATIONS.

Substance.	Grams taken.	Method.	Percentage of N found.	Theory.
Nitrourea. ....	1.0000	Nitrometer	13.17	13.33
Nitrourea. ....	1.0000	Nitrometer	13.20	
Nitroguanidine. ....	1.0000	Nitrometer	13.32	13.46
Nitroguanidine. ....	0.3030	B. & J. (a)	13.54	
Nitroguanidine. ....	0.3580	B. & J. (a)	13.42	
Tetryl. ....	2.5000 (b)	Nitrometer	4.71	4.88
Tetryl. ....	2.5000 (b)	Nitrometer	4.74	
Tetryl. ....	2.5000 (c)	Nitrometer	4.71	
Tetryl. ....	2.5000 (c)	Nitrometer	4.74	
Tetryl. ....	0.9000 (c)	B. & J. (a)	4.87	
Tetryl. ....	0.9000 (c)	B. & J. (a)	4.90	

(a) = Berl and Jurrissen method.

(b) = Commercial tetryl.

(c) = Tetryl crystallized from benzene.

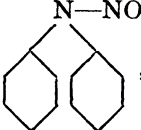
### Observations on Results.

The nitrometer results are consistently somewhat low. This is due to a slight action of the sulfuric acid on these nitrocompounds and consequent loss of a small amount of gas, before forcing the substance into the nitrometer bulb. The results with the decomposition flask are all well within experimental error.

The nitrometer and especially the decomposition flask method of Berl and Jurrissen are well adapted for the determination of nitrogen in nitrocompounds where the nitro group is attached to the carbon through a nitrogen atom.<sup>1</sup>

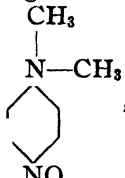
<sup>1</sup> It is, perhaps, of interest to note that these compounds may be considered as esters of nitric acid,  $\text{NO}_2\text{—O—R}$  in which the oxygen atom connecting R with  $\text{NO}_2$  is replaced by NH. It recalls the work of E. C. Franklin who has shown that  $\text{K—NH—H}$  is base and acetamide,  $\text{C}_2\text{H}_5\text{O—NH—H}$  is an acid in anhydrous ammonia.—EDITOR

In the nitric esters we have  $\equiv \text{C}-\text{O}-\text{NO}_2$ , or the  $\text{NO}_2$  group linked to carbon through an oxygen atom. In the nitrocompounds under discussion,  $\equiv \text{C}-\text{N} \begin{cases} \text{H or CH}_3 \\ \text{NO}_2 \end{cases}$ , the nitro group is linked to carbon through a nitrogen atom. If we now turn to the nitrous esters  $\equiv \text{C}-\text{O}-\text{NO}$  we find an  $\text{NO}$  group linked to carbon through oxygen. By analogy we should expect nitroso compounds in which the nitroso group is linked to carbon through nitrogen likewise to yield its nitroso nitrogen in the nitrometer reaction.

Nitroso diphenylamine, , was selected as a compound of

this type. As sulfuric acid causes a rather violent reaction upon this substance the decomposition flask was used for this reaction. The results obtained were 6.97, 6.94, and 7.05% N, theoretical 7.07% N. Again allowing for impurities in the sample, these results are well within experimental error. The gas formed was examined in the same manner as in previous experiments, and was identified as nitric oxide.

To allay any apprehension that this might be a general reaction for all

nitroso compounds, *p*-nitrosodimethylaniline, , was selected

as one which had the nitroso group attached directly to carbon. Sulfuric acid likewise acts rather violently on this substance, but on completing the reaction with mercury, about one-sixth the theoretical quantity of gas was formed, and only a trace of this was absorbed by ferrous sulfate solution. This also shows that the nitroso group must be attached to the carbon atom through nitrogen, in order that the nitroso nitrogen may be determined by the nitrometer reaction.

A curious anomaly occurs when it is attempted to determine nitrogen in urea and guanidine nitrates in the nitrometer in the usual manner, *i. e.*, by dissolving in a small quantity of water, introducing into bulb, then adding the sulfuric acid, etc. Results were obtained varying from 13.3 to 15.6% N if all the gas formed is considered as  $\text{NO}$ . This was not the case, as on a few qualitative tests the gas showed considerable  $\text{CO}_2$  and  $\text{N}_2$  besides the  $\text{NO}$ . Theoretical nitrate nitrogen for urea nitrate is 11.38% and for guanidine nitrate 11.48%. Both these compounds must first be converted into their respective nitrocompounds before they can

be determined in the nitrometer. This is easily accomplished by slowly adding a weighed sample (e. g., 1 g.) of the nitrate to 20 cc. conc. sulfuric acid cooled to  $0^{\circ}$  and kept at this temperature until all the nitrate is dissolved. This converts the nitrate into the nitrocompound, which may then be introduced into the nitrometer, the cup washed with 10 cc. additional sulfuric acid, and the reaction completed in the usual manner. This method will yield practically theoretical results for the nitrates.

### Summary.

1. The nitrometer has been used for a great variety of analytical operations, in which a definite quantity of a gas is evolved, not soluble to a very considerable extent in the liquid from which it is evolved, and not acting upon mercury.

2. The characteristic nitrometer reaction has been used only for nitrous and nitric acid, their salts and esters.

3. Further evidence is given that the nitrometer reaction does not liberate NO from true nitrocompounds in which the nitro group is linked directly to the carbon atom.

4. Characteristic reactions for nitrocompounds are given and evidence is produced that nitrocompounds in which the nitro group is attached to carbon through nitrogen give most of these reactions.

5. The application of the true nitrometer reaction is extended for the determination of nitrogen of the  $\text{NO}_2$  and NO groups in nitroamines and nitrosoamines in which the respective groups are attached to carbon through nitrogen.

6. The nitrometer reaction may be used as a means of ascertaining whether the  $\text{NO}_2$  and NO group is attached directly to the carbon or through a nitrogen atom.

7. An anomaly is noted in which the nitrates of urea and guanidine cannot be determined in the nitrometer in the usual manner. They must be converted into their respective nitrocompounds first, after which they may be readily determined.

EXPLOSIVES CHEMICAL LABORATORY,  
BUREAU OF MINES,  
PITTSBURGH.

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[CHEMICAL LABORATORY OF THE NEW YORK STATE HOSPITAL.]

## THE COMPOSITION OF NEUROKERATIN.

By BURT E. NELSON.

Received September 9, 1916.

Neurokeratin, which was first isolated by Kühne, is supposed to be the chief characteristic constituent of the neuroglia cells of the brain, and of the axilemma and outer sheath of the medullary substance of the nerve trunks. It is classed chemically with the general group of keratins;

which form the characteristic constituents of the hair, hoofs, horn, nails, shells, scales and other tissues of epiblastic origin, and whose chief characteristics among the other classes of proteins are their insolubility in water, salt solutions, acid and weak alkali solutions, their indigestibility in pepsin-hydrochloric acid, and their relatively high content of sulfur in the molecule.

Widely varying analytical figures have been reported by other observers<sup>1</sup> for the elementary composition of this substance, the discrepancies doubtless arising from different methods used in isolating it, and the analysis of impure products. It was with a view of obtaining more trustworthy results that the following analysis was undertaken:

The material used was the total protein residue from several lots of brains of patients diagnosed as having general paresis, senile dementia (with plaques), and dementia praecox, which had been previously extracted with alcohol, ether, and warm water, for the lipid and extractive matters.

Previous to these extractions the minced brain tissues had been allowed to remain in 85% alcohol for two months, to insure thorough coagulation and hardening of the proteins. This final dried protein residue was finely ground and digested in an incubator at blood heat, six times with one hundred times its amount of pepsin-salt-hydrochloric acid mixture, for twenty-four hours each, or three times after the cessation of the biuret reaction. It was then similarly digested five times with 0.1% solution of sodium hydroxide to dissolve nucleins and finally extracted again with alcohol and ether and dried at a gentle heat.

It formed a pale yellowish, light powder, showing no further changes on treatment with solvents (which removed at most only traces of soluble matters) and had a mineral ash content of 0.22 to 0.25%.

Elementary analysis for carbon and hydrogen, by combustion of one-half gram lots gave:

C, 54.86%, 54.73%, 54.95%, and 54.95%; H, 7.33%, 7.30%, 7.18%, and 7.33%.

Nitrogen determinations by the Kjeldahl method, on half-gram lots, using no catalyzing agent, and continuing the digestions for three hours after the solutions were colorless, gave

N, 13.12%, 13.24%, 13.16%, and 13.16%.

Similarly, sulfur determinations on one-gram lots, by combustion in oxygen gas in a closed calorimeter bomb, gave

Sulfur, 1.37%, and 1.40%.

Phosphorus was entirely absent.

The average elementary analysis of our material is therefore

C, 54.87%; H, 7.28%; N, 13.17%; S, 1.38%; O, 23.07%; and ash, 0.23%.

<sup>1</sup> Hammersten, *Physiol. Chemie*, 6; Argiris, *Z. physiol. Chem.*, 54, 86-94 and ourselves, *Psychiatric Bull. New York State Hospitals*, 9, No. 3.

This is an unusually low nitrogen, and especially sulfur, content for a keratin, although closely similar to the figures obtained in our previous analyses. The other elementary analyses of this substance have varied as follows:

C, 56 to 58.5%; H, 7.25 to 9.00%; N, 11.5 to 14.0%; and S, 1.63 to 2.31%.

In an attempt to further learn the structural make-up of this protein molecule, a single partition of the nitrogen content among the several amino acids, etc., was made, using a slight modification of Van Slyke's method.

2.715 g. of the neurokeratin were hydrolyzed by heating for sixty hours with diluted hydrochloric acid, or until the total amino nitrogen was constant. The resulting solution was then analyzed and gave:

Total hydrolyzed nitrogen 0.3570 g. (100%), ammonia nitrogen 0.01875 g., uncorrected arginine nitrogen 0.01344 g., melanin nitrogen 0.0518 g., total nitrogen precipitated by phosphotungstic acid 0.0896 g., total nitrogen not precipitated by phosphotungstic acid 0.18984 g., amino nitrogen precipitated by phosphotungstic acid 0.0800 g., total amino nitrogen not precipitated by phosphotungstic acid 0.0900 g., and total sulfur precipitated by phosphotungstic acid 0.0378 gram.

By calculation we arrive at figures for the various products of hydrolysis as follows:

Ammonia nitrogen.....	5.24%
Melanin nitrogen.....	14.51%
Arginine nitrogen.....	2.692%
Cystine nitrogen.....	4.40%
Histidine nitrogen.....	6.279%
Lysine nitrogen.....	11.729%
Nitrogen from one or all of pyroline, oxyproline, or tryptophane..	27.95%
Nitrogen from one or all of glutamic acid, aspartic acid, tyrosine, leucine, isoleucine, alanine, or glycocoll.....	25.21%
Total.....	98.01%
Error and loss.....	1.99%

The results of this single fractionation cannot, however, be accepted as final. They do indicate, however, that most of the sulfur exists in the form of cystine, which is characteristic of keratins as a class.

All of the above figures representing the ultimate elementary analysis of this material are in fairly close accord with some previously obtained by us in a similar manner, so the reasons for the discrepancies in published results must, as previously surmised, lie in variations in the purity of the neurokeratins analyzed. The indigestibility of our protein, its insolubility in dilute alkali, and its freedom from phosphorus, would seem to surely eliminate the chance for an admixture with brain globulins, other proteins, or nucleins. Some elastic tissue from the finer cerebral vessels might possibly, however, be present.

The low nitrogen content, as before stated, is peculiar for any protein



of this class, being indeed more nearly like that in the case of some mucin substances, while the sulfur found more nearly coincides with the amount found in most globulins, rather than in keratins.

A. Argiris<sup>1</sup> obtained on analysis of his neurokeratin:

C, 56.60%; H, 7.15 and 7.40%; N, 14.16%; and S, 2.24 to 2.31%, calculated to the ash-free material.

His analysis of the hydrolytic products also gave different results, but was performed after the older methods. On the other hand, one of the analyses quoted by Hammersten gives nitrogen as low as 11.5%.

Whether or not the long standing of the tissues in 85% alcohol and the subsequent extraction with boiling alcohol, might have permanently rendered other of the proteins indigestible and insoluble, or what portion, if any, of similar indigestible proteins might possibly have been left from the cerebral vessels, we are unable to say definitely; but these last then must probably also have been present in preparations of neurokeratin obtained by Kühne and Chittenden's method.

### Conclusions.

Neurokeratin, as obtained by us, is a protein of unusually low nitrogen and sulfur content, as compared with more commonly known keratins, and appears to differ from these latter also in the structural make up of its molecule.

BINGHAMTON, N. Y.

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[CONTRIBUTION FROM THE CHEMISTRY SECTION OF THE IOWA AGRICULTURAL EXPERIMENT STATION.]

## AN ACCURATE AERATION METHOD FOR THE DETERMINATION OF ALCOHOL IN FERMENTATION MIXTURES.

By ARTHUR W. DOX AND A. R. LAMB.

Received August 28, 1916.

### Introduction.

A great deal of work has been done upon methods for the determination of ethyl alcohol by physical means, principally the specific gravity, the index of refraction, or the boiling point of alcoholic solutions. Physical methods, however, are all open to the same objection, *viz.*, that the presence of any other substance than ethyl alcohol in the solution tested will always cause incorrect—usually high—results. The production of alcohol in fermentation processes, in whose products it is generally desired to estimate the alcohol, is invariably accompanied by the formation of by-products in greater or less amount, even in pure yeast cultures. Many of these other products are volatile, and cannot be separated from the alcohol by distillation, especially in dilute solutions. The estimation

<sup>1</sup> *Loc. cit.*

of the alcohol in such a mixture by physical methods must therefore be very difficult to free from error.

Chemical methods have not received nearly so much attention, perhaps because the physical methods generally consume less time. However, the list of interfering substances should not be nearly so long in the case of the determination of ethyl alcohol by oxidation to acetic acid, since it would include only volatile substances which yield a volatile acid on oxidation. The latter method should therefore be more reliable, and may perhaps be susceptible of development to as great a degree of accuracy.

It is not the purpose of this paper, however, to enter into a discussion of the relative merits of physical and chemical methods, but merely to present the results of a considerable experience with chemical methods for the determination of alcohol, which may be of value to others engaged with fermentation problems.

### The Oxidation of Alcohol.

In the oxidation method there are two possible sources of error, which may be considered separately. The first, which is common to all methods, lies in the difficulty in quantitatively removing the alcohol from the original fermented solution, and in getting it into a convenient volume for oxidation. Direct distillation of a fermented solution is likely to be troublesome, especially when nearly all of the solution must be distilled over in order to get all of the alcohol into the distillate. Distillation with steam in the usual manner will volatilize all of the alcohol only after a very long time, and it is difficult to concentrate the large distillate without losing a considerable amount of the alcohol. The second possible source of error is in the oxidation itself, where the oxidation may be incomplete, yielding aldehyde, or may go too far, with the production of carbon dioxide and water. Other substances than alcohol, which might yield a volatile acid as an oxidation product, might also be present.

The most commonly used oxidizing agent is a sulfuric acid solution of potassium dichromate. Potassium permanganate solution has not often been suggested. A recent paper by Evans and Day<sup>1</sup> has shown that varying amounts of oxalic acid and carbon dioxide are formed in the oxidation, in addition to the acetic acid. The sulfuric acid-dichromate method was used by Hehner,<sup>2</sup> and by Benedict and Norris,<sup>3</sup> who determined the amount of dichromate reduced, and by Dupre,<sup>4</sup> who distilled and titrated the acetic acid formed. Various modifications of Dupre's method have been used by Suzuki, Hastings, and Hart,<sup>5</sup> and by Hart,

<sup>1</sup> THIS JOURNAL, 38, 375-381 (1916).

<sup>2</sup> *Analyst*, 12, 25 (1887).

<sup>3</sup> THIS JOURNAL, 20, 293 (1898).

<sup>4</sup> *J. Chem. Soc.*, 20, 495 (1867).

<sup>5</sup> *J. Biol. Chem.*, 7, 431-438 (1910).

Hastings, Flint, and Evans,<sup>1</sup> in work on cheese, and by Hart and Willaman,<sup>2</sup> and by Dox and Neidig,<sup>3</sup> in work on corn silage.

### Experimental Part.

**Oxidation Trials.**—Dupre's method, as originally published,<sup>4</sup> is unsupported by data checking it against known alcohol solutions, and has apparently not been standardized by other workers who have used the method. Since a reliable and accurate method was necessary for use in the silage investigations in progress in this laboratory, a careful study of Dupre's method was begun. It seemed that the distillation and titration of the acetic acid formed would be much more trustworthy than the determination of the reduced dichromate, as done by Benedict and Norris,<sup>4</sup> since various organic substances might reduce the dichromate, while the formation of a volatile acid in the oxidation would be much less likely to occur. Therefore the oxidation of standard alcohol solutions by Dupre's method was first studied.

The standard alcoholic solutions were made by weighing out about 10 g. of redistilled, nearly absolute, alcohol, and making up to exactly 1000 cc. with CO<sub>2</sub>-free distilled water. The densities of the original alcohol and of the dilute solutions were determined with a Sprengel pycnometer, and the strength of the dilute alcohol solutions calculated. Samples were taken with a carefully calibrated pipet.

Various mixtures of sulfuric acid and dichromate have been used by other workers, but the exact proportions seem to be of minor importance. The oxidizing solution decided upon and used in most of this work was made up in the following proportions: 10 g. K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, 20 g. H<sub>2</sub>SO<sub>4</sub>, 70 g. CO<sub>2</sub>-free distilled water. Oxidation in a pressure flask in a boiling water bath was first tried. It was soon found that 30 minutes' oxidation would give as good results as 3 hours. Later it was found that if the solution was merely allowed to stand in the distilling flask a few minutes at room temperature, before distillation, the results obtained were fully as accurate. The reaction seems to be complete in a very few minutes on heating, during the time necessary to bring the solution in the distilling flask to the boiling point. In the case of oxidation at room temperature, the first few cubic centimeters of the distillate sometimes have a slight odor of acetaldehyde, but this small loss is apparently no greater than the loss attendant upon transferring the liquid from the pressure flask to the distilling flask in the case of oxidation with heat.

Dupre and later workers with his method have reduced the excess dichromate in the oxidizing solution with zinc, before distillation. This

<sup>1</sup> *J. Agr. Res.*, 2, 193 (1914).

<sup>2</sup> *THIS JOURNAL*, 34, 1619 (1912).

<sup>3</sup> *Iowa Agr. Exp. Sta., Research Bull.* 7 (1912) and 16 (1914).

<sup>4</sup> *Loc. cit.*

extra step is not only entirely unnecessary, but it is often a source of trouble in the distillation. Therefore it has not been done in this work.

The distillation of the volatile acid from the oxidizing solution is carried on carefully over a free flame, using an asbestos board with a small circular opening for the bottom of the distilling flask. The combination of a glass bead with two small pieces of pumice stone in the distilling flask has been found the most satisfactory preventive of both bumping and foaming during the distillation. If care is taken not to permit the volume of liquid in the distilling flask to become low enough to allow sulfuric acid to be carried over, the distillation gives no trouble whatever. If barium hydroxide solution is used for the titration, the presence of any sulfuric acid in the distillate will at once be detected. The oxidizing solution is repeatedly distilled with additions of  $\text{CO}_2$ -free distilled water, until the last titration is 0.5 cc. of a decinormal solution, or less. This is generally after four or five distillations. If care is taken, the error due to carbon dioxide is negligible. Some representative data secured on this part of the process are shown in Table I.

TABLE I.—OXIDATION OF KNOWN ALCOHOL SOLUTIONS.

Conditions.	Calc. g. alcohol.	Found g. alcohol.	Recovery. %.
Oxidation at 100°, 30-40 min.....	0.238	0.236	99.2
	0.238	0.235	98.7
	0.257	0.257	100
	0.257	0.256	99.6
Oxidation at room temperature.....	0.238	0.237	99.6
	0.257	0.256	99.6
	0.257	0.257	100

Only when the method of oxidation had been perfected, and reliable results in that part of the process assured, were the more uncertain preliminary steps studied.

**Distillation of Alcohol Solutions.**—Previous investigators have concentrated the alcohol solution obtained from steam distillation by successive redistillations, distilling off each time about one-half to three-fourths of the volume in the flask. This method is very tedious and far from quantitative. Bacon,<sup>1</sup> of the Bureau of Chemistry, has shown that it is possible, by nearly saturating the alcohol solution with common salt, to distill off all the alcohol in the first one-fifth of the volume distilled, Bacon's suggestion was carried further in this work, by adding the salt to the original solution to be distilled with steam, thus liberating both the alcohols and the volatile acids much more readily, and getting them over practically completely in the first 500 cc. of distillate. It is noteworthy that although lactic acid was present in the solution, no hydrochloric acid was liberated. Solid phenolphthalein was added to the distillate, the volatile acids titrated and fixed; and the alcoholic solution easily

<sup>1</sup> U. S. Dept. Agr., Bur. Chem., *Circ.* 74 (1911).

concentrated in one or two distillations with salt to a convenient volume for oxidation. A few typical results obtained with known solutions by this method are shown in Table II. This table also shows the result obtained by the concentration of a known solution from 500 cc. to 50 cc. with the use of salt, to compare with steam distillation with salt followed by concentration. In one distillation shown the salt used was ammonium sulfate.

TABLE II.—DISTILLATION AND OXIDATION OF KNOWN ALCOHOL SOLUTIONS.

Conditions.	Calc. g. alcohol.	Found g. alcohol	Recovery. %.
Distilled and concentrated with NaCl.....	0.238	0.210	88.2
	0.238	0.225	94.6
	0.238	0.216	90.8
Concentrated only, with NaCl.....	0.238	0.228	96.6
Distilled and concentrated with $(\text{NH}_4)_2\text{SO}_4$	0.238	0.218	91.6

Steam distillation of alcohol solutions generally gives just such variable results as are shown in this table. It is evident that the greatest loss of alcohol in this method occurs during the distillation with steam.

#### Aeration Method.

Since the saturation of an alcoholic solution with a soluble salt brings about the liberation of the alcohol by distillation so readily, it seemed probable that alcohol could be volatilized by aeration at room temperature from a similarly saturated solution. Ammonium sulfate was chosen as a suitable salt for the purpose, and was found more efficient than sodium chloride. A known amount of alcohol in 100 cc. of water was placed in a Drexel gas-washing bottle with 80 g. of ammonium sulfate. This was connected to a series of two bottles, each containing 50 cc. of oxidizing solution, which were followed by a flask containing a definite amount of 0.1 *N* barium hydroxide solution. A soda-lime tube and a guard bottle containing oxidizing solution were placed at the beginning of the train, and a stream of air was drawn through at a moderate rate with a water pump. This method gave at first more or less variable results. It was necessary to determine the amount of volatile acid, exclusive of carbon dioxide, which had been caught by the barium hydroxide solution, and to distill off the rest of the acetic acid from the oxidizing solution. However, the volatilization of the alcohol was found to be complete in about 8 hours' aeration, and the amount of alcohol recovered averaged from 90% to 96%.

Benedict and Norris<sup>1</sup> make the statement that concentrated sulfuric acid takes up alcohol as readily as it does water. Therefore a bottle containing 20 cc. of the acid was substituted for the oxidizing solution, and the barium hydroxide and soda-lime were eliminated. After aeration the sulfuric acid was carefully added to 100 cc. of saturated solution of

<sup>1</sup> *Loc. cit.*

potassium dichromate, oxidized, and distilled as before. More accurate and more uniform results were obtained than before, and other advantages were secured. As the alcohol is not oxidized until after the aeration is completed, there is no danger of loss of volatile acid. The sulfuric acid takes up the alcohol more completely than does the oxidizing solution. The alcohol is brought into a small volume, and may be left in that condition indefinitely, if not convenient to make the oxidation at once. A smaller number of bottles is necessary in the train, and less attention is required.

Instead of a regular gas-washing bottle as a container for the sulfuric acid, it is preferable to use an ordinary 100 cc. graduated cylinder, fitted with a rubber stopper carrying an inlet and an outlet tube. The inlet tube may be slightly constricted at the lower end, or a bulb with small perforations, similar to a Folin bulb, may be blown at the end, to secure still more efficient absorption. However, it is necessary in any case to use two cylinders of sulfuric acid, in order to secure the most complete recovery of the alcohol. It seems that this is not because the stream of air is too large or too fast, but because the reaction between the alcohol and the sulfuric acid is reversible, and therefore a small amount of the alcohol passes over into the second cylinder. The recovery of alcohol was increased by 1%-2% when the second cylinder was first used.

A few representative results showing the average accuracy of the method are given in Table III. In nearly all cases, the oxidation was at room temperature.

TABLE III.—THE DETERMINATION OF ALCOHOL IN KNOWN SOLUTIONS BY THE AERATION METHOD.

Conditions.	Calc. g. alcohol.	Found g. alcohol.	Recovery. %.
Oxidizing solution used to fix alcohol. . .	0.238	0.227	95.4
	0.238	0.226	95.0
	0.238	0.229	96.2
Concentrated H <sub>2</sub> SO <sub>4</sub> used to fix alcohol.	0.257	0.248	96.5
	0.257	0.250	97.3
	0.257	0.252	98.1
	0.257	0.254	98.8
	0.103	0.101	98.0
	1.620	1.594	98.4
	0.0202	0.0201	99.5

The aeration train, as now made up, consists of a guard bottle of oxidizing solution, followed by the saturated ammonium sulfate solution containing the alcohol, and by two cylinders of concentrated sulfuric acid, the first containing about 18 cc. and the second 8-10 cc. of acid. The rate at which the air is drawn through is about 25 liters per hour. The aeration is generally complete in 8-10 hours, but slightly higher results are obtained by aeration at a slower rate for 24 hours, minimizing the spattering of the sulfuric acid. After the aeration is complete, the

sulfuric acid is mixed with 10–15 g. of dichromate in water in the distilling flask, and the cylinders well rinsed with CO<sub>2</sub>-free water. The mixture is allowed to stand about 15 minutes, and then distilled as described above.

The ammonium sulfate used should be as nearly neutral as possible. The commercial C. P. salt sometimes contains a considerable amount of bisulfate.

It is interesting to know that volatile fatty acids cannot be determined by aeration, either with ammonium sulfate or sodium chloride, although they distill over from a saturated salt solution at 100° faster than the alcohol.

Quite large amounts of alcohol, up to two grams, can be determined accurately by this method. Larger amounts can be determined by using a smaller sample. In the presence of half a gram of alcohol or more, the sulfuric acid and dichromate solutions must be mixed carefully and cooled.

The entire determination requires from 12 to 30 hours, but requires personal attention amounting in time to less than one hour. The results obtained are as accurate and more trustworthy than those obtained by any other method applicable to fermentation mixtures which is known to the authors. This method has been used for the determination of alcohol in various kinds of silage with very satisfactory results.

**Interfering Substances.**—Acetone is oxidized but slightly under the conditions of this method. It is carried over by aeration, but most of it distills unchanged from the oxidizing solution. About 0.6 g. of acetone yielded only 0.003 g. of acetic acid. If oxidized for 2 or 3 hours in a pressure flask at 100°, however, it is nearly all oxidized to acetic acid.

Certain esters, especially ethyl acetate, interfere with the determination of alcohol by this method, but these may be determined separately.

Acetaldehyde is readily volatilized and oxidized to acetic acid, but aldehydes generally occur in fermentation mixtures only in small quantities as intermediate products.

Methyl alcohol is almost completely oxidized under these conditions to carbon dioxide and water. Some recent investigators have apparently overlooked this fact in dealing with mixtures of alcohols, which were oxidized and determined as the corresponding acids by the Duclaux method. Only 0.012 g. of methyl alcohol was recovered as formic acid from 0.185 g. by aeration and oxidation.

According to Thorpe and Holmes,<sup>1</sup> pyridine is not changed by the sulfuric acid-dichromate mixture, allyl alcohol is completely oxidized to carbon dioxide and water, and methyl acetate yields both carbon dioxide and acetic acid. They also state that ethyl alcohol yields constantly

<sup>1</sup> *J. Chem. Soc.*, 85, 1 (1904).

0.5% of its weight as carbon dioxide. The correction may be applied, if desired. The presence of toluol does not effect the accuracy of the method, as the toluol is not oxidized.

### Summary.

The determination of ethyl alcohol by oxidation with sulfuric acid-dichromate solution has been carefully studied. It is considered that the best results are obtained when the alcohol is finally determined by distillation and titration of the acetic acid formed.

The preparation of the solution by distillation, even from a saturated salt solution, is tedious and troublesome and far from quantitative.

The alcohol solution may be saturated with ammonium sulfate and the alcohol carried over into concentrated sulfuric acid by a current of air at room temperature. The alcohol-sulfuric acid solution may then be mixed with a solution of potassium dichromate and the acetic acid distilled off at once. Results accurate within 1.5% of the amount used have been obtained by this method.

Necessary precautions and interfering substances are discussed.

AMES, IOWA.

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[FROM THE N. Y. STATE DEPARTMENT OF HEALTH LABORATORIES, ALBANY, N. Y.]

## THE EFFICIENCY OF THE AERATION METHOD FOR DISTILLING AMMONIA; IN ANSWER TO CERTAIN CRITICISMS.

By PHILIP ADOLPH KOBER.

Received September 3, 1916.

From his "Comparative Study of Aeration and Heat Distillation in the Kjeldahl Method for the Determination of Nitrogen" Falk<sup>1</sup> concludes that "the aeration procedure in the ordinary Kjeldahl method for nitrogen very often gives inaccurate and therefore unreliable results, and should not be used."

This conclusion is based on his failure to remove all of the ammonia by aeration. Dillingham<sup>2</sup> has also recorded failure to obtain satisfactory results for the same reasons, while Bock and Benedict<sup>3</sup> and Greenwald<sup>4</sup> report great variations in the results of their determinations without accounting for them.

Accordingly, I have studied carefully the records of these observers in their published articles in the hope of discovering the sources of error, whether in the method or in the manner in which it was used.

Falk attempts to employ the results of Davis, as confirmatory data, in saying that:

<sup>1</sup> THIS JOURNAL, 38, 916 (1916).

<sup>2</sup> *Ibid.*, 36, 1310 (1914).

<sup>3</sup> *J. Biol. Chem.*, 20, 47 (1915).

<sup>4</sup> *Ibid.*, 21, 61 (1915).



"Davis found aeration to give unsatisfactory results in the determination in cottonseed meal and proposed to heat the solution during aeration."

But Davis<sup>1</sup> said that: "If the flask \* \* \* were placed in an asbestos box \* \* \* the solutions kept warm an hour and a half," and "the results checked with results obtained by ordinary Kjeldahl." Heat was only proposed if larger amounts of substance were used and then only for "fifteen minutes," and in conclusion, "the method described by Kober if modified as described will give good results with other nitrogen containing bodies."

The reason for this modification is apparent, as Davis states on page 56, that "the stream of air drawn by the ordinary glass pump was not strong enough to carry over the ammonia by the time the solution cooled," thus showing that he realized the necessity for strong aeration. However, it is quite unnecessary to heat, because a little longer aeration accomplishes the same result.

In the experiments of Gill and Grindley<sup>2</sup> mentioned by Falk, only the analysis of one substance failed to yield satisfactory results. When compared to a large number of accurate results which they obtained this is of little significance. These observers strongly recommended the aeration procedure for the distillation of ammonia in urea and urine estimations.

Finally, in citing the work of others Falk relies for most of his support on Dillingham,<sup>3</sup> but he overlooks the essential fact that to Dillingham's technic can be attributed all his unsatisfactory results. He used a flask of large diameter (800 cc. capacity), and thereby spread out and decreased the height of the liquid through which the ammonia should pass and almost destroyed the efficiency of his aeration. That the higher the column for a given liquid, the more efficient the aeration, is too obvious to need but passing mention. Dillingham's attention was called to this oversight two years ago, but no re-investigation, although promised, has thus far appeared. Whether any other defects in his technic are involved it is impossible to say.

*To sum up, then, the only support in the literature found by Falk, was one instance with a defective pump (Davis), and another instance with an unsuitable flask (Dillingham).*

Considering Falk's results independently, the following points are to be noted:

1. Disagreement in the results obtained by aeration.
2. With one or two exceptions, the amount of ammonia undistilled was nearly proportional to the total amount present originally.

<sup>1</sup> THIS JOURNAL, 31, 56 (1909).

<sup>2</sup> *Ibid.*, 31, 1249 (1909).

<sup>3</sup> *Ibid.*, 36, 1310 (1914).

3. That the amount of aeration varied as much as 39%, and even 30%, in a series of distillations "testing before and after the run."

4. That the speed of aeration during a run was never tested, and is therefore unknown.

It is clear from these four points that the main cause of the discrepancies in the results was poor aeration.

That the aeration was weak at the Harriman laboratory, due to inadequate water supply for the overcrowded rooms, was found by the writer personally and is shown by the fact that Falk's collaborator in this paper, Sugiura, under more favorable conditions in former years, when less water was used for other purposes, did get good checks for the aeration procedure.<sup>1</sup>

It is a very simple matter to test out the efficiency of aeration by adding Nessler's solution to the Kjeldahl residue, as was recommended in a previous paper,<sup>2</sup> but this seems not to have been considered by Falk, even though with steam distillation an increase in titration alone is no test for ammonia. Dissolved alkali from the glass condenser, if used, will alone account for such a phenomenon.

To re-check the cardinal points the following demonstration was made: An ordinary Kjeldahl distillation was run with an extra absorption bottle.

After aeration Nessler's reagent was added to the Kjeldahl flask and Graves' reagent to the extra absorption bottle. The negative result with the residue in the Kjeldahl flask leaves no question that all the ammonia had been aerated over, and since there was no ammonia in the extra absorption bottle it was proved conclusively that all the ammonia was in the first absorption bottle and was completely absorbed.

Where there is an abundance of air supply, as in institutes particularly equipped with air compressors and vacuum systems, and in all laboratories where the "micro" form of apparatus is used, which requires much less air, no such aeration difficulty is found. That in many laboratories water suction pumps are inefficient was brought out by Pennington<sup>3</sup> and accounts for the failure of Boussingault in 1850 to apply successfully the aeration method using only 56 liters an hour, while Folin employing 600-700 liters an hour was the first to demonstrate successfully that ammonia can be distilled by aeration from weakly alkaline solutions and absorbed quantitatively.

The positive results for urea estimations by Henriques<sup>4</sup> and Gammeltoft are not mentioned by Falk. He also fails to cite the work of Potter<sup>5</sup> and Snyder who state that "as to accuracy and ease Kober's statements have

<sup>1</sup> THIS JOURNAL, 35, 1603 (1913).

<sup>2</sup> Kober and Graves, *Ibid.*, 35, 1601 (1913).

<sup>3</sup> THIS JOURNAL, 32, 561 (1909).

<sup>4</sup> *Skand. Archiv. Phys.*, 25, 166 (1911); *Bohr-Gedachnesschrift*.

<sup>5</sup> *J. Ind. Eng. Chem.*, 17, 226 (1915).

been confirmed." Furthermore, a large number of other workers who have used aeration in one form or another for distillation of ammonia have been completely overlooked.

It is of interest to note that while Falk was completing his article, Van Slyke<sup>1</sup> and Cullen, at the Rockefeller Institute, published a paper showing that the aeration of ammonia even in "micro" amounts is so thoroughly established that it follows a definite law, namely, that of a mono-molecular reaction, and given certain factors the time necessary for complete distillation could be calculated. Furthermore, even for very small amounts of ammonia Van Slyke and Cullen conclude that "*the accuracy attainable is limited only by that of the measurements and standard solutions.*"

It might be assumed that this statement applies to the micro and not to the macro process under discussion, but it would be difficult to explain, if ammonia in micro amounts can be aerated over and absorbed, why larger amounts should not be distilled over if aeration is used in proportion.

In regard to the publications of my collaborators and myself, Falk gives the impression that only comparatively few satisfactory results were obtained, ignoring the fact that the aeration method has been used by us for regular work exclusively for eight years and has been checked by many assistants. This work comprises several thousand<sup>2</sup> duplicate and triplicate analyses which agree closely, but only protocols of which have been published. Thus it is evident that the failure of aeration results to agree indicates defective technic.

### Summary.

To insure accurate results in distilling ammonia by aeration it is necessary to use:

1. A sufficient volume of air.
2. As high a column but as low a volume of liquid as is convenient.
3. A saturated solution of pure sodium hydroxide in adequate excess.<sup>3</sup>

An impure alkali containing or producing sulfite is liable to cause error because of the sulfur dioxide evolved and carried over into the standard acid before the acid of the Kjeldahl mixture is completely neutralized.

4. Potassium hydroxide must not be used because the difficultly soluble potassium sulfate which separates may carry down ammonia by occlusion or as a double salt. Errors of 10% may be caused in this way but potassium sulfate as ordinarily used is not sufficient to produce appreciable error.

<sup>1</sup> *J. Biol. Chem.*, **24**, 117 (1916).

<sup>2</sup> Levene and Kober, *Am. J. Physiol.*, **23**, 328 (1909); Saccharine Report, U. S. Dept. of Agriculture, Referee Board of Consulting Scientific Experts, from the Herter Lab. The statements in these publications that the total nitrogen estimations were made according to the Kjeldahl-Gunning process are not quite correct; they were practically all distilled according to the aeration method.

<sup>3</sup> Kober and Graves, *THIS JOURNAL*, **35**, 1600 (1913).

5. The complete removal of the ammonia from the Kjeldahl mixture should be tested with Nessler's solution. The precaution of Van Slyke to run the aeration slowly or at half speed for the first minute or two may be an advantage.

#### Addendum.

After sending in this paper for publication I learn that recently a number of other investigators have tried the aeration method and found it accurate. I. K. Phelps and H. W. Daudt, from the Bureau of Chemistry, Washington, D. C., reported favorably on the method at the Urbana meeting of the Society. B. S. Davisson, E. R. Allen and B. M. Stubblefield<sup>1</sup> were able, with a powerful aeration, to remove and absorb small amounts of ammonia from large volumes of solution accurately, using only magnesium hydroxide as an alkali.

ALBANY, N. Y.

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[CONTRIBUTION FROM THE SPRECKLES AGRICULTURAL RESEARCH LABORATORY.]

### PRESENCE OF NITRITES AND AMMONIA IN DISEASED PLANTS. ITS SIGNIFICANCE WITH REGARD TO CROP ROTATION AND SOIL DEPLETION.<sup>2</sup>

By P. A. BONCQUET.

Received July 3, 1916.

The present study was made independently from the discussion now at large concerning the presence of nitrites in plants.<sup>3</sup> It is not the intention of the writer to decide the above contentions, but only to make known some facts which may throw new light on the controversy.

**Nitrites in Diseased Beets.**—During previous work *Bacillus morulans*, Boncquet,<sup>4</sup> was found to be an inhabitant of the sieve tubes of sugar beets affected with Curly Leaf.<sup>5</sup> Moreover it was established that the organism was not confined to the disease of beets called Curly Leaf, but that it was connected with a great variety of irregular foliage types representing various forms of leaf wrinkling, curling and distortions.<sup>4</sup> The same organisms were also isolated in cultures from the interior of leaves of beets

<sup>1</sup> *J. Ind. Eng. Chem.*, **8**, 896 (1916).

<sup>2</sup> The writer is greatly indebted to the Spreckles Sugar Company for the splendid facilities placed at his disposal in the realization of this investigation.

<sup>3</sup> Klein, *Bot. Centbl. Beihefte, I Abt.*, n 1, **30**, 141-166 (1915); *E. S. R.*, **33**, 627; Oso and Sekine, *Ibid.*, *I Abt.*, **32**, 146-147 (1914); *E. S. R.*, **33**, 627; Maze, *Compt. rend. soc. Biol.*, [Paris] **78**, 98-102 (1915); *E. S. R.*, **34**, 627.

<sup>4</sup> Boncquet, *Bacillus morulans* n. sp. A bacterial organism which inhabits the sieve tubes of sugar beets and related plants. Its characters and significance. A thesis presented for the degree of Doctor of Philosophy at the University of California.

<sup>5</sup> Ralph E. Smith and P. A. Boncquet, "New Light on Curly Top of the Sugar Beet," *Phytopathology*, **5**, 103-107 (1915).

affected with the diseases called Mottled Leaf, Black Leaf, and Black Tip of beets.<sup>1</sup>

As the biochemical investigations of *B. morulans* proved this organism to be a most vigorous nitrate reducer,<sup>2</sup> it was in logical sequence to test for nitrites any plant tissue in which the organism was found as a facultative parasite. These investigations were crowned with success every time the slightest irregularity revealed the presence of bacteria in the plant tissues. On the other hand, absolutely smooth and sterile tissue gave, without any exception, a perfectly negative result. Not even a trace of nitrite could be detected in perfect, normal leaves. In some cases, however, even a slight irregularity in the vein distribution indicated traces of nitrites which could be detected in the leaf juices.

**Ammonia in Diseased Beets.**—The reducing power of *B. morulans* Bonquet is not confined to the reduction of nitrates to nitrites, but the bacillus is found able to reduce nitrates as far as ammonia. In consequence of this, the same tissues which were found to contain nitrites were also tested for ammonia. The presence of the organism likewise decided whether the leaf juice contained ammonia or not. Under no circumstances was ammonia detected, where the leaf was found strictly nonpathological. Under some circumstances some leaves contained more ammonia than nitrites in comparison to other beets. This was especially true if the leaves had been separated from the crown of the plant, or if the plant had been taken from the soil and left to wilt. The reduction was sometimes found so far advanced that only ammonia could be detected, all nitrites having been reduced.

**Nitrites and Ammonia in Tobacco Leaves Affected with the "Mosaic Disease" (filtrable virus).**—An exceedingly small streptococcus was found to be connected with this disease. Its biochemical functions proved to be vigorous in reducing power. Nitrates in the test tubes were easily converted to nitrites and even ammonia. Thereupon the juices of diseased leaves were also tested for nitrites. It was found that normal tobacco leaves did not give the test for nitrites. Conversely, the juice of all diseased leaves gave a very strong nitrate reduction; ammonia was also detected.

**Nitrites in Potato Leaves and Tubers.**—A streptococcus called for the present *Streptococcus solani* n. sp. was found uniformly in certain potato vines and leaves. The fact that the micrococcus was found to be a most active nitrate reducer naturally suggested the presence of nitrites in the plant juices. It was found that all potato plants of the leaf type containing the micrococcus give a vigorous nitrite reaction in their expressed

<sup>1</sup> Ralph E. Smith and P. A. Bonquet, "Connection of a Bacterial Organism with Curly Leaf of the Beet Sugar," *Phytopathology*, 5, 335-342 (1915).

<sup>2</sup> Bonquet, *Loc. cit.*

leaf sap. Slight traces of ammonia were also detected. On the other hand, leaves and tissues of plants which did not possess any abnormalities and of a totally different leaf type, give negative results. This pathological condition of the potato has not been described distinctly from the pathological standpoint, owing to the fact that the plant appears normal in the broadest sense. The writer has at present a great deal of evidence that this condition is connected with the so-called "brown streak" and with the "blossom abortion" of potatoes, all of which appear to be different symptoms of one and the same disturbance, brought about by *Streptococcus solani*. The plants which gave the most pronounced nitrite test were growing very luxuriantly. The leaves were dark green, crinkled, however, and light revealed irregular patches of lighter green all over the leaf; more or less of the nature of those patches to be observed in the mosaic disease of tobacco. The tubers, however, were not affected with the regular "brown streak" but rather with a disturbance better called "brown or petrified heart." This petrification consists of the cells of the heart of the potato being slightly incrustated with a light cement. Patches of necrotic cells are distributed irregularly throughout the hard mass. Numerous conglomerates of streptococci were abundantly observed in and around the brown tissues. Although the nitrites were very abundant in the leaf tissues, the affected tubers gave only traces of nitrites. This absence of nitrites with the presence of an abundant bacterial flora is easily understood when chemical analysis revealed only traces of nitrates present in the tubers.

**Nitrates in Other Plants.**—Several other plants which showed abnormalities in leaf or stem structure were examined for their nitrite content. It was found that some individual alfalfa, bean and *Malva rotundifolia* plants gave a decided nitrite reaction. The intensity of the reaction ran parallel with the severity of the sickly conditions in which the plants were found. However, a yellow color was not always a sign that the plant contained nitrite or ammonia. It was rather the abnormal plant development from a structural standpoint, like the deformities of leaf, dwarfing, curling and distorting that manifested the disturbance.

All plant juices from plants where these abnormalities had been found, although obtained aseptically, were able to reduce nitrates to nitrites when inoculated in nitrite-free peptone tubes. At the same time a considerable growth of bacteria was obtained, which proved on subsequent inoculation to be very active nitrite reducers.

#### **Significance of the Presence of Nitrites in Plant Tissues.**

**Relation of the Internal Bacterial Flora to Soil Depletion and Crop Rotation.**—The presence of nitrites in plants, at least in all cases which the writer had under investigation, is due to the reducing power of the internal bacterial flora in the tissues. Nitrites have not been detected

in any plant tissue which was normal in the strictest sense of the word. The pathological disturbance is brought about by a partial and local nitrogen starvation of the tissues, and further by the mechanical laceration of local foci, where the bacteria in some cases, by their active growth, were forming metastatic ulcers.

The local and partial nitrogen starvation in the leaves around nitrate-reducing foci explains the mozaic nature of the leaf diseases in which an abundance of nitrite is detected. The foci of infection, found at the headgate of some secondary leaf veination, explains just why that region in the leaf which is under the control of the infected headgate, suffers most from starvation and why it is pale yellow while other regions of the leaf, not controlled by a diseased headgate in the veination, are abundantly supplied with nitrates and consequently develop the heavy green color so characteristic of nitrogen abundance.

The mechanical laceration of infected foci is the cause of a local arrest of growth in the veins and this arrest of growth brings about leaf distortion. In some other cases the internal bacterial flora is uniformly distributed throughout the plant tissues. In consequence of this the symptoms are also uniform, and result in dwarfing and arrested growth as in "little leaf" diseases.

The pathological condition due to the disturbance of a nitrate-reducing bacterial flora in the tissues, may even be without any visible symptoms. Nevertheless, in these cases the nitrite-containing juices extracted aseptically from diseased plants when inoculated in nitrite-free peptone tubes, always brings about a vigorous nitrate reduction, with an abundant growth of nitrate-reducing bacteria. Tissues free from nitrate on inoculation give a sterile tube with no tract of nitrite to be detected.

**Significance to Soil Depletion and Crop Rotation.**—Further studies and field observations have led the writer to believe that the nitrite content of plants and consequently the internal bacterial activity which brings the nitrate-reduction about, has a fundamental bearing on certain cases of soil depletion. This is especially believed to be true in potato fields. A field was observed which had been planted with potatoes for more than fifteen years. Nearly every vine was affected with nitrogen starvation due to internal bacterial reduction.

On the other hand, the soil in which the potatoes were growing was abundantly supplied with nitrates. The analysis showed more than sixty parts per million of soluble nitrates. In this abundance of plant food the potatoes gave a poor yield. It seems, especially from observations on beet fields, that the virulence of nitrate-reducing bacteria as invaders of plant tissues is increased by lack of crop rotation and consequently reduces the yield in some cases to such a point that the reduction is attributed to soil depletion.

### Summary.

Nitrites in plants in the cases observed were due to the reducing power of the internal bacterial flora. This reduction is the cause of nitrogen starvation of plants affected with some peculiar diseases. This nitrogen starvation may occur even when plants are growing on a soil where nitrates are abundant. The internal bacterial flora of plants with its nitrogen-reducing power may be a direct factor in soil depletion where crop rotation is not practiced, owing to the increased virulence and invading power of reducing bacteria. It is believed that lack of crop rotation provides soil organisms a better opportunity to establish themselves in the veins and tissues of plants by means of adaptation.

SPRECKELS, CAL.

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### NEW BOOK.

**Annual Reports of the Progress of Chemistry for 1915.** Issued by the Chemical Society.  
Vol. XII. London, 1916. Pp. viii + 268. Sold by D. Van Nostrand Company.  
\$2.00 net.

In 1905 the Chemical Society of London inaugurated the publication of this series of annual reports of the progress of chemistry. Issued usually in the late spring, they aim at giving an epitome of the most important work of the preceding year. For the busy chemist who would know what is taking place in other branches of chemistry than his own special field, they are invaluable; within his field he will find them at least interesting and suggestive. Prepared so soon after the close of the year, they naturally lack perspective, and they may often give undue prominence to topics for which the reviewer has a particular bias, but this detracts little from their value. The reviewers of the different fields are for the most part specialists and investigators, which lends interest and value to their work. The contents of the present volume are: General and Physical Chemistry, H. M. Dawson. Inorganic Chemistry, E. C. C. Baly. Organic Chemistry: Part I, Aliphatic Division, J. C. Irvine; Part II, Homocyclic Division, F. L. Pyman; Part III, Heterocyclic Division, A. W. Stewart. Analytical Chemistry, G. Cecil Jones. Physiological Chemistry, F. G. Hopkins. Agricultural Chemistry and Vegetable Physiology, N. H. J. Miller. Mineralogical Chemistry, T. V. Barker. In time past the American Chemical Society has published occasional similar reviews in *THIS JOURNAL*. Such duplication of preparation is unwise to say the least, but it is a pity that some arrangement cannot be made whereby such reviews in the English language may be put in the hands of every member of both societies, and we should add that the Society of Chemical Industry ought also to coöperate in the work.

JAS. LEWIS HOWE.



# THE JOURNAL

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### American Chemical Journal

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY.]

#### THE OCCLUSION OF HYDROGEN BY A PALLADIUM CATHODE.

BY DONALD P. SMITH AND FREDERICK H. MARTIN.

Received August 14, 1916.

The occlusion of hydrogen by palladium, whether from the gas directly or during electrolysis, has been the subject of numerous investigations. In particular, the changes in the electrical resistance of the metal brought about by this occlusion have been studied by Graham,<sup>1</sup> Dewar,<sup>2</sup> Knott,<sup>3</sup> Bruchietti,<sup>4</sup> Krakau,<sup>5</sup> McElfresh,<sup>6</sup> Fischer,<sup>7</sup> Sieverts<sup>8</sup> and Wolf.<sup>9</sup>

As a result of these investigations it has been established that an increase in the specific resistance of the metal results from the occlusion and that, at least between thirty and about nine hundred and eighty volumes, the increase in resistance is approximately proportional to the hydrogen taken up.

With regard, however, to the relation between the resistance and the

<sup>1</sup> *Proc. Roy. Soc. London*, **17**, 212 (1869).

<sup>2</sup> *Proc. Camb. Phil. Soc.*, **3**, 207 (1878).

<sup>3</sup> *Proc. Roy. Soc. Edinb.*, **12**, 181 (1884).

<sup>4</sup> *L'Elettricista*, Nov., 1893.

<sup>5</sup> *Z. physik. Chem.*, **17**, 689 (1893).

<sup>6</sup> *Cont. Jeff. Phys. Lab.*, **1**, 305 (1903).

<sup>7</sup> Dissertation, Leipzig, 1906; *Ann. Phys.*, [4] **20**, 503 (1906).

<sup>8</sup> *Internat. Zeits. Metallog.*, **3**, 36 (1912).

<sup>9</sup> *Z. physik. Chem.*, **87**, 575 (1914).

quantity of occluded gas, which obtains for the high degrees of occlusion reached in palladium cathodes when electrolysis is long continued, we have only the observations of Fischer.<sup>1</sup> These are remarkable in that the last portions of gas, which, since they are again spontaneously evolved as soon as the current is interrupted, he termed "supersaturation" hydrogen, produce no effect upon resistance, although they cause an expansion of the metal proportionally greater than that produced by the occlusion in its earlier stages. Since the increased effect of the "supersaturation" hydrogen upon the volume was also found by Thoma,<sup>2</sup> this lack of effect upon resistance raises certain questions as to the nature of the states of "saturation" and "supersaturation."

In order, if possible, to obtain further information upon these questions and upon the phenomena of occlusion generally, the following experiments were undertaken. They consisted in observing the changes in the electrical resistance and in the cathode potential of palladium wires during their cathodic occlusion of hydrogen from 2 *N* sulfuric acid. As a control of the conditions of electrolysis, the applied voltage and the current were also observed, and occasional measurements were made of the anode potential.

### Experiments.

The electrolytic cell consisted of separate cathode and anode vessels, the former of which is shown in Fig. 1. Here A is the inlet for the electrolyte and B the outlet. The palladium wire *e, f, g, h*, about 10 cm. long, is fused at each end to two other palladium wires, X and Y, which pass through the rubber stoppers C, C and are soldered outside to copper wires of 3.26 mm. diameter, which form the leads of a Kelvin bridge. D is a siphon which connects through an intermediate vessel with the reference electrode. To make possible the observation of the cathode potential during electrolysis, without the introduction of an error due to the ohmic fall of potential, this siphon terminates in a small orifice held directly against the cathode. The principle is that of the capillary-tip siphon of Luggin and Haber,<sup>3</sup> and the modifications necessary to keep the wire cathode in place during its expansion with absorption of hydrogen will be clear from Fig. 1a. To make the distribution of current at the cathode symmetrical the latter is connected to battery through the branched lead *j, j*.

In order to diminish changes in the temperature or composition of the electrolyte in the constricted cathode chamber, the liquid was made to flow through the cell during electrolysis at the rate of about four liters in twenty-four hours, while to guard against its depolarizing influence,

<sup>1</sup> Dissertation, Leipzig, 1905; *Ann. phys.*, [4] 20, 503 (1906).

<sup>2</sup> *Ibid.*, 3, 69 (1889).

<sup>3</sup> Haber, *Z. physik. Chem.*, 32, 207 (1900).

all air was displaced by nitrogen from the closed system of vessels through which the electrolyte circulated. The cell and a glass coil through which the electrolyte first passed were contained in a large oil thermostat which maintained a temperature of  $25 \pm 0.01^\circ$ . The platinum anode was enclosed in a porous cup to preclude the possibility that platinum might find its way to the cathode.<sup>1</sup>

The measurements of electrical resistance had an accuracy of about one part in 6000 for the higher resistances encountered in the later portions of the experiments with small palladium wires, where alone results of interest were obtained, while the measurements of e. m. f. were made with the potentiometer. Potentials refer to a mercurous sulfate electrode with 2 *N* sulfuric acid, which varied during the investigation by less than one millivolt.

The electrolyte used throughout was 2 *N* sulfuric acid, for the preparation of which chemically pure acid was redistilled in quartz and diluted with water of conductivity between 1.0 and  $1.2 \cdot 10^{-6}$ . The concen-

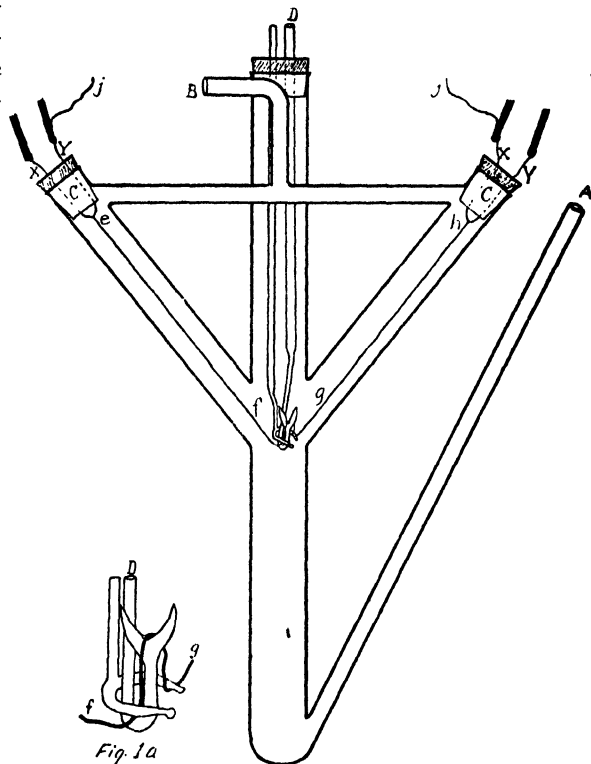


Fig. 1.—Cathode vessel.

tration, which corresponded to a specific gravity of 1.0605 at  $21^\circ$ , was occasionally controlled by titrating against normal hydrochloric acid, obtained by the method of Hulett and Bonner.

During the course of the experiments palladium from three different sources was employed. One sample, G, of Table II, was a piece of foil obtained from a German dealer and drawn into wire for the present purpose; another lot, A, was obtained ready-drawn from an American dealer

<sup>1</sup> See J. Tafel, *Z. physik. Chem.*, 50, 641 (1905); J. Tafel and B. Emmert, *Ibid.*, 52, 349 (1905).

and the third variety, P, was prepared in this laboratory from commercial palladium by employing in succession the customary methods for the separation of this metal, precipitations with hydrogen sulfide, ammonium thiocyanate and mercuric cyanide being repeated.

Before use each wire, from whatever source, was ignited *in vacuo* at  $830^{\circ}$  for from four to ten hours to expel any occluded gas and to anneal the metal. Evacuation to a pressure of 1 mm. of mercury, or less, was effected by means of a lift pump, a vessel of finely divided silver being interposed between the pump and wire in order to guard against the vapor of mercury, which Ramsay<sup>1</sup> has shown to exert an inhibitive action upon the occlusion of hydrogen by palladium. Except in one instance a new wire was taken for each experiment.

The initial reading of resistance was made as soon as possible after the cell had filled with electrolyte, and before electrolysis had begun. It was found that no change occurred even in the course of several days, until the charging circuit had been closed. The other measurements were made at such intervals as may be seen from Table I, in which are given in full the observations taken in one of the six experiments with varied charging current. In four other experiments a constant current was employed. Saturation was in general considered, to have been attained when the curve of resistance as a function of current-time (see Fig. 3), had become horizontal within the limits of measurement, but in several instances the charging was much prolonged, and in Expt. 5, electrolysis was continued for six days after the attainment of apparent constancy, without causing any further change.

TABLE I.  
Experiment No. 5.

Time.	Applied <sup>2</sup> voltage.	Current.	Cathode potential.		Resistance.
			C. F. <sup>3</sup>	C. S. <sup>4</sup>	
8.50 A.M., Jan. 18	1.82 volts	0.2 mil. amps.	0.6150	0.5950 volt	.....
9.00 A.M., Jan. 18	....	stopped	....	....	1.446 ohm.
9.25 A.M., Jan. 19	....	started	....	....	1.446
9.30 A.M., Jan. 19	1.82	0.2	0.6300	0.5850	1.514
10.00 A.M., Jan. 19	2.26	0.2	0.6800	0.6100	1.528
10.20 A.M., Jan. 19	2.15	0.2	0.6810	0.6120	1.536
10.35 A.M., Jan. 19	2.35	0.3	0.7040	0.6100	1.552
10.50 A.M., Jan. 19	2.57	0.5	0.7160	0.6110	1.588
11.05 A.M., Jan. 19	2.82	0.6	0.7270	0.6120	1.630
11.20 A.M., Jan. 19	3.63	0.8	0.7470	0.6100	1.688
11.35 A.M., Jan. 19	3.98	0.9	0.7474	0.6100	1.756
11.50 A.M., Jan. 19	4.46	1.0	0.7615	0.6100	1.832

<sup>1</sup> *Phil. Mag.*, [5] 38, 209 (1894).

<sup>2</sup> In this column is given the potential difference between the poles of the electrolytic cell, properly termed, applied voltage until the interruption of the current.

<sup>3</sup> "Current flowing."

<sup>4</sup> "Current stopped."

TABLE I (continued).

Time.	Applied voltage.	Current.	Cathode potential.		Resistance.
			C. F.	C. S.	
12.05 P.M., Jan. 19	5.18	1.2	0.7740	0.6385	1.924
2.30 P.M., Jan. 19	2.00	0.2	0.7030	0.6350	2.034
2.45 P.M., Jan. 19	2.07	0.2	0.7100	0.6330	2.041
3.00 P.M., Jan. 19	2.17	0.3	0.7180	0.6340	2.047
3.15 P.M., Jan. 19	2.34	0.3	0.7300	0.6420	2.063
3.30 P.M., Jan. 19	2.61	0.4	0.7420	0.6470	2.080
3.45 P.M., Jan. 19	2.84	0.5	0.7520	0.6500	2.096
4.00 P.M., Jan. 19	3.69	0.8	0.7720	0.6700	2.183
4.15 P.M., Jan. 19	4.00	0.9	0.7770	0.6700	2.207
4.30 P.M., Jan. 19	4.48	1.0	0.7840	0.6790	2.248
4.45 P.M., Jan. 19	5.19	1.2	0.7950	0.6840	2.270
10.00 A.M., Jan. 20	2.08	0.2	0.7650	0.6665	2.466
10.15 A.M., Jan. 20	2.15	0.2	0.7710	0.6660	2.466
10.30 A.M., Jan. 20	2.24	0.3	0.7790	0.6690	2.466
10.45 A.M., Jan. 20	2.39	0.3	0.7910	0.6720	2.466
11.00 A.M., Jan. 20	2.63	0.4	0.8050	0.6750	2.466
11.15 A.M., Jan. 20	2.87	0.5	0.8170	0.6820	2.466
11.30 A.M., Jan. 20	3.69	0.8	0.8410	0.6920	2.462
11.45 A.M., Jan. 20	4.01	0.9	0.8475	0.6990	2.460
12.00 A.M., Jan. 20	4.49	1.0	0.8550	0.7050	2.464
12.15 P.M., Jan. 20	5.19	1.2	0.8690	0.7100	2.464
12.20 P.M., Jan. 20	....	0.2	....	....	2.472
2.15 P.M., Jan. 20	2.08	0.2	0.7685	0.6670	2.504
2.30 P.M., Jan. 20	2.15	0.2	0.7750	0.6675	2.502
2.45 P.M., Jan. 20	2.24	0.2	0.7800	0.6710	2.502
3.00 P.M., Jan. 20	2.39	0.3	0.7900	0.6720	2.502
3.15 P.M., Jan. 20	2.64	0.4	0.8130	0.6780	2.498
3.30 P.M., Jan. 20	2.88	0.5	0.8240	0.6830	2.496
3.45 P.M., Jan. 20	3.72	0.8	0.8510	0.6950	2.486
4.00 P.M., Jan. 20	4.07	0.9	0.8600	0.7035	2.478
4.15 P.M., Jan. 20	4.59	1.0	0.8665	0.7050	2.476
4.30 P.M., Jan. 20	5.24	1.2	0.8800	0.7050	2.462
5.00 P.M., Jan. 20	....	0.2	....	....	2.484
7.15 P.M., Jan. 21	2.15	0.2	0.8330	0.6750	2.467
8.20 A.M., Jan. 22	2.17	0.2	0.8510	0.6750	2.470
9.10 A.M., Jan. 22	....	0.8	....	....	....
9.15 A.M., Jan. 22	....	0.8	....	....	2.458
9.20 A.M., Jan. 22	3.81	0.8	0.9480	0.6750	2.430
9.50 A.M., Jan. 22	3.82	0.8	0.9480	0.6710	2.420
10.20 A.M., Jan. 22	3.82	0.8	0.9480	0.6650	2.428
10.50 A.M., Jan. 22	3.83	0.8	0.9475	0.6580	2.422
11.20 A.M., Jan. 22	3.83	0.8	0.9500	0.6525	2.416
12.00 A.M., Jan. 22	3.84	0.8	0.9480	0.6450	....
1.15 P.M., Jan. 22	....	1.0	....	....	....
2.15 P.M., Jan. 22	4.59	1.0	1.0185	0.6570	2.416
3.30 P.M., Jan. 22	4.58	1.0	0.9970	0.6450	2.414
4.40 P.M., Jan. 22	....	0.3	....	....	....
4.45 P.M., Jan. 22	....	0.3	....	....	2.434

TABLE I (*continued*).

Time.	Applied voltage.	Current.	Cathode potential.		Resistance
			C. F.	C. S.	
9.00 A.M., Jan. 24	2.40	0.3	0.9735	0.6065	2.440
11.00 A.M., Jan. 24	2.40	0.3	0.9735	0.6065	2.440
2.00 P.M., Jan. 24	2.40	0.3	0.9590	0.5920	2.440
2.10 P.M., Jan. 24	....	0.6	....	....	....
7.00 P.M., Jan. 24	3.48	0.6	1.0530	0.6050	2.408
8.45 A.M., Jan. 25	3.52	0.6	1.092	0.6170	2.402
8.50 A.M., Jan. 25	....	1.0	....	....	....
2.40 P.M., Jan. 25	4.63	1.0	1.1370	0.6140	2.388
7.10 P.M., Jan. 25	....	0.4	....	....	....
7.15 P.M., Jan. 25	2.99	0.4	0.9950	0.5870	2.424
9.30 A.M., Jan. 26	3.10	0.4	1.0900	0.5870	2.414
9.35 A.M., Jan. 26	....	stopped	....	....	....
9.50 A.M., Jan. 26	1.37	000	....	0.5650	2.456
10.05 A.M., Jan. 26	1.33	000	....	0.5570	2.472
10.30 A.M., Jan. 26	1.29	000	....	0.5400	2.482
10.45 A.M., Jan. 26	1.27	000	....	0.5380	2.490
11.00 A.M., Jan. 26	1.26	000	....	0.5350	2.494
11.15 A.M., Jan. 26	1.25	000	....	0.5450	2.496
11.30 A.M., Jan. 26	1.23	000	....	0.5700	2.498
11.45 A.M., Jan. 26	1.06	000	....	0.5590	2.500
12.00 A.M., Jan. 26	1.03	000	....	0.5540	2.502
12.30 P.M., Jan. 26	0.97	000	....	0.5560	2.504
1.00 P.M., Jan. 26	0.93	000	....	0.5490	2.508
1.30 P.M., Jan. 26	0.90	000	....	0.5650	2.508
2.00 P.M., Jan. 26	0.86	000	....	0.5610	2.508
2.30 P.M., Jan. 26	0.80	000	....	0.5440	2.508
3.00 P.M., Jan. 26	0.75	000	....	0.5430	2.508
3.30 P.M., Jan. 26	0.68	000	....	0.5425	2.512
4.00 P.M., Jan. 26	0.68	000	....	0.5470	2.512
4.30 P.M., Jan. 26	0.68	000	....	0.5435	2.512
5.00 P.M., Jan. 26	0.70	000	....	0.5500	2.512
5.30 P.M., Jan. 26	0.71	000	....	0.5800	2.512
6.00 P.M., Jan. 26	0.72	000	....	0.5670	2.512
7.00 P.M., Jan. 26	0.73	000	....	0.5700	2.512
8.00 P.M., Jan. 26	0.73	000	....	0.5750	2.512
9.00 P.M., Jan. 26	0.74	000	....	0.5750	2.514
10.00 P.M., Jan. 26	0.73	000	....	0.5750	2.514
8.00 A.M., Jan. 27	0.73	000	....	0.5790	2.514
10.00 A.M., Jan. 27	0.73	000	....	0.5890	2.514
12.00 A.M., Jan. 27	0.75	000	....	0.5910	2.515
2.00 P.M., Jan. 27	0.75	000	....	0.5930	2.516
4.00 P.M., Jan. 27	0.76	000	....	0.5930	2.516
8.00 A.M., Jan. 28	0.73	000	....	0.5820	2.520
9.30 A.M., Jan. 28	0.73	000	....	0.5830	2.520
9.31 A.M., Jan. 28	....	started	....	....	....
9.32 A.M., Jan. 28	3.22	0.6	0.9040	0.5290	2.518
2.15 P.M., Jan. 28	3.39	0.6	1.0200	0.6350	2.390
7.00 P.M., Jan. 28	3.46	0.6	1.0540	0.6220	2.382

TABLE I (continued).

Time.	Applied voltage.	Current.	Cathode potential.		Resistance.
			C. F.	C. S.	
8.00 A.M., Jan. 29	3.48	0.6	1.0980	0.6000	2.382
1.00 P.M., Jan. 29	....	1.0	....	....	....
7.00 P.M., Jan. 29	4.65	1.0	1.1750	0.5980	2.376
7.05 P.M., Jan. 29	....	0.6	....	....	....
9.00 A.M., Jan. 31	3.54	0.6	1.1550	0.5820	2.390
9.05 A.M., Jan. 31	....	stopped	....	....	....
9.07 A.M., Jan. 31	1.49	000	....	0.5740	2.406
9.30 A.M., Jan. 31	1.32	000	....	0.5440	2.458
10.00 A.M., Jan. 31	1.27	000	....	0.5170	2.474
10.30 A.M., Jan. 31	1.24	000	....	0.5025	2.486
11.00 A.M., Jan. 31	1.21	000	....	0.5000	2.492
11.30 A.M., Jan. 31	1.19	000	....	0.5070	2.496
12.00 A.M., Jan. 31	1.13	000	....	0.5070	2.500
1.00 P.M., Jan. 31	1.01	000	....	0.5070	2.504
2.00 P.M., Jan. 31	0.88	000	....	0.5070	2.506
7.00 P.M., Jan. 31	0.68	000	....	0.5150	2.512
8.00 A.M., Feb. 1	0.73	000	....	0.5810	2.514
1.00 P.M., Feb. 1	0.72	000	....	0.5740	2.515
8.15 A.M., Feb. 2	0.69	000	....	0.5550	2.516

The principal results with regard to resistance may be summarized as follows:

(1) All palladium wires increased in resistance during electrolysis by more than 56%, finally reaching a value which remained unaltered by prolonged charging, but which appeared to vary irregularly from wire to wire.

(2) Wires of 0.1 mm. diameter or less, and the ribbon of Expt. 12, which was 0.018 mm. thick and 0.57 mm. wide, showed a further increase of resistance after the interruption of electrolysis.

(3) With the small wires and ribbon there was also found a change of resistance whenever the intensity of the charging current was altered either during the later stages of occlusion or after the attainment of saturation.

(4) The larger wire of Expt. 11 could not be made to exhibit the effects noted under (2) and (3).

The variability of the saturation resistance, referred to under (1), is shown in the fifth column of Table II, where the highest resistance attained with each wire is expressed as per cent. increase of the original resistance.

The effect mentioned in (2) may be seen from the last column of Table II, and is further illustrated by Fig. 2, where each curve shows the change of resistance which occurred after the interruption of electrolysis in the case of a wire which had already reached a constant resistance with the current flowing.

The dependence of resistance on current, noted in (3), is displayed by Fig. 3, where are given portions of the curves of resistance, as dependent upon current-time, for four wires. At A on each curve may be seen the

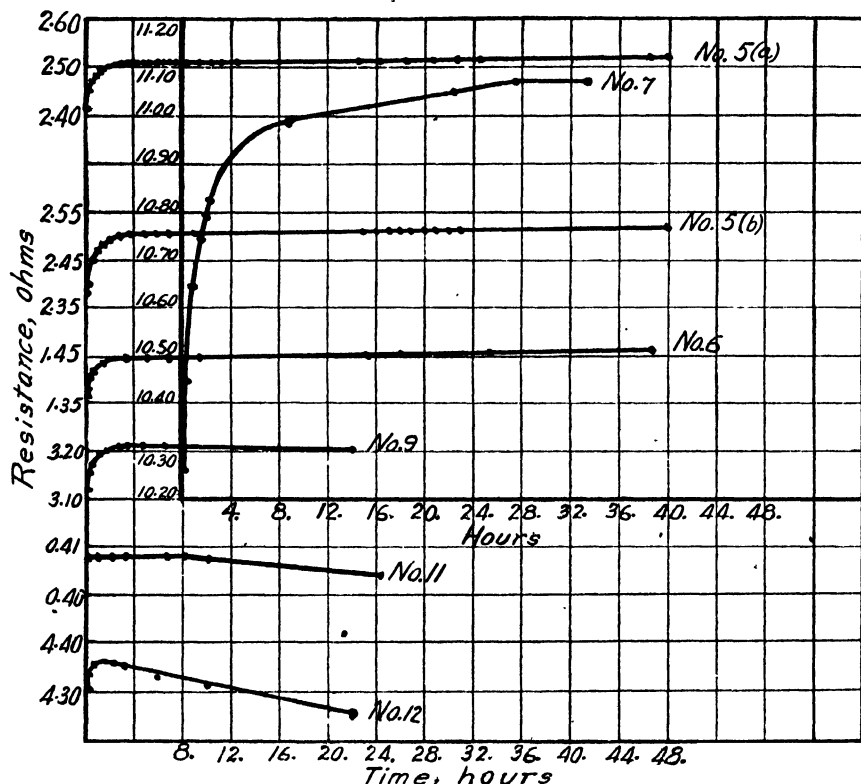


Fig. 2.—Change of resistance after interruption of current.

drop in resistance induced by an increase of current, while at B occurs an increase of resistance produced by diminution of current. In the case of No. 3 the current was raised at A from 0.8 to 1.1 milliamp. and was reduced at B to 0.2 milliamp.

TABLE II.

Expt. No.	Material.	Diameter.	Current.	Constant resistance.	Increase.
2	G	0.1	0.1	72.4	...
3	P	0.1	0.2	63.0	1.3
4	P	0.1	0.2	57.7	...
5	A	0.1	1.2	> 73.2	< 0.7
6	A	0.1	1.2	74.7	1.3
7	G	0.05	0.5	56.7	12.6
8	A	0.1	0.2	62.5	2.5
10	A	0.1	0.1	61.9	2.6
11	P	0.32	1.1	56.9	0.0
12	P	ribbon	0.8	57.7	0.5



The conduct of the large wire, mentioned in (4), is shown by Curve 11 of Fig. 2. When this wire was again charged, after the loss of resistance shown in the figure, it recovered exactly its former maximum resistance in six hours and retained it unaltered until the current was again interrupted forty-three hours later. The resistance curve obtained after this second interruption was entirely similar to that shown.

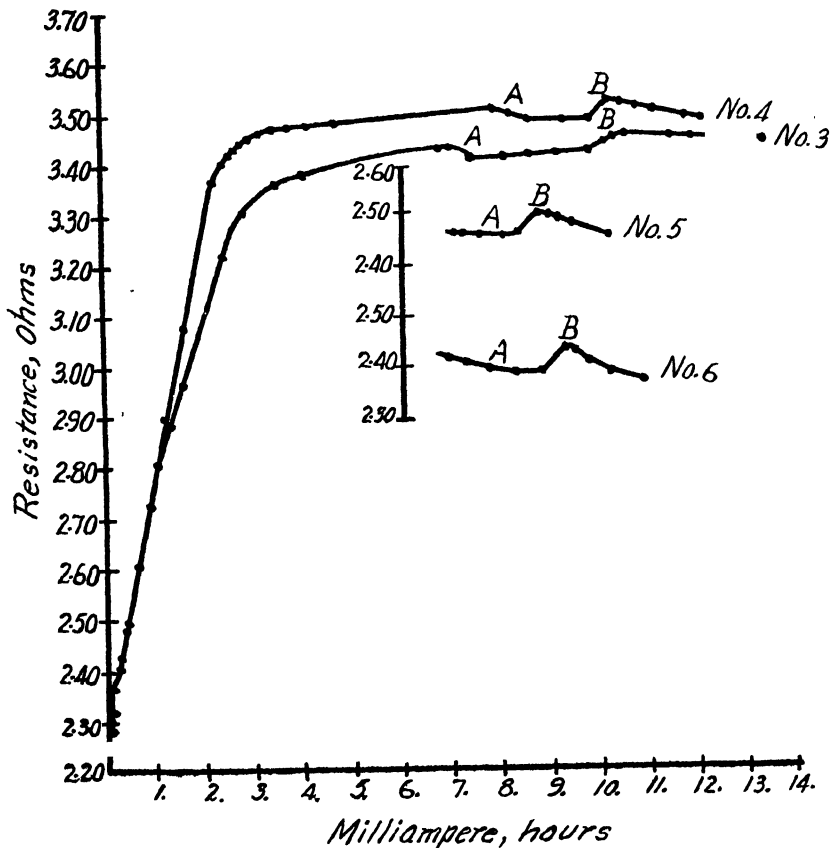


Fig. 3.—Dependence of resistance upon current during electrolysis.

The results of the observations made upon the cathode potential were as follows: The potential, in every case, rose steadily so long as electrolysis was continued. Upon the interruption of the current at the end of the first charging of a palladium wire there always occurred the series of changes shown in the first part of Fig. 4, consisting of a sharp drop, followed by a pronounced recovery and then by a gradual decline. When a wire was repeatedly charged to constant resistance, the recovery of potential became less marked with each succeeding interruption of elec-

trolysis, as may be seen from the eight successive curves for the same cathode given in Fig. 4. The initial drop of potential, preceding the re-

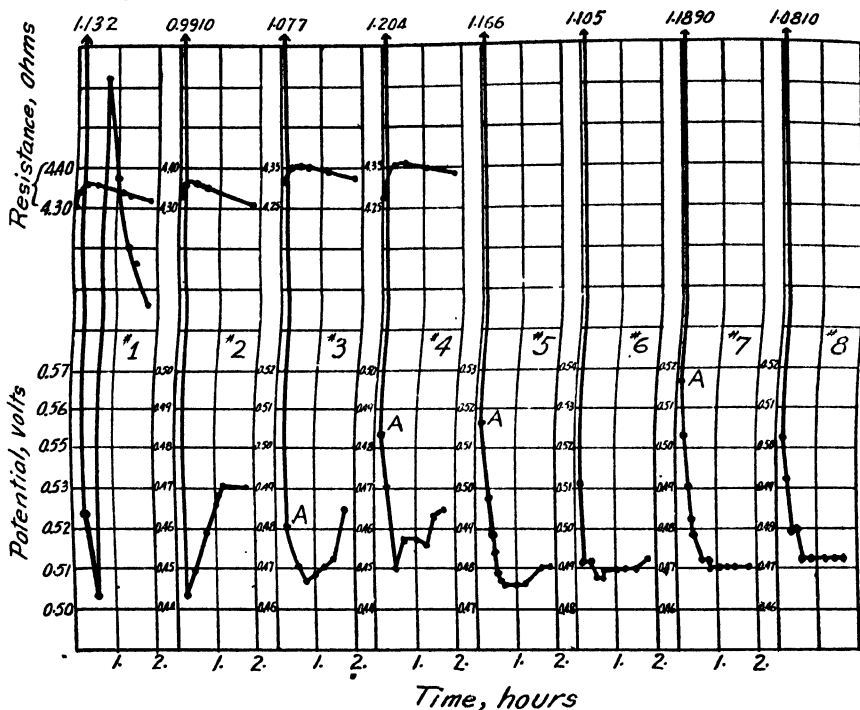


Fig. 4.—Changes of potential and resistance for successive interruptions.

covery, appeared to consist of two parts. For the first reading, taken as soon as possible after the interruption, instead of corresponding to chance

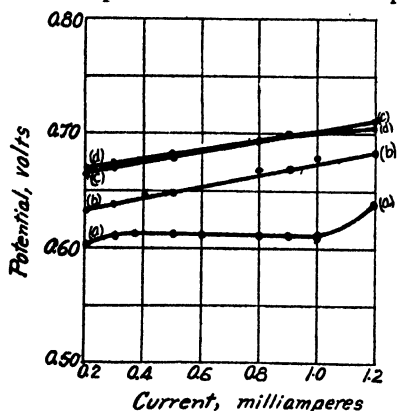


Fig 5.—First readings of potential after interruption of current, Expt. 5.

positions upon the falling branch of the curve, showed marked regularity, as may be seen from Fig. 5. Here the points upon Curve *a* represent the first readings for successive interruptions of electrolysis during the first charging of Wire No. 5, while Curves *b*, *c* and *d* correspond to three subsequent chargings of the same wire. The regularity with which these values increase with increasing occlusion, together with the form of the potential-time curves, seen best in Nos. 4, 5 and 7 of Fig. 4, seem to show that the point *A* of these last is a well-

defined potential, determined by the state of occlusion in the surface of the metal.

For comparison two similar experiments were made with copper wires of 0.1 mm. diameter, drawn from electrolytic copper. In these the initial resistance was observed, and the charging circuit was closed, before the introduction of the electrolyte. No change of resistance was found either during electrolysis or after its interruption, nor did the wires show brittleness or any other change upon their removal from the cell. The potential during electrolysis altered in the manner shown by Curves *a*, *b* and *c* of Fig. 6, which correspond to successive chargings with the same wire. After the interruption of the current the potential fell off in a perfectly regular manner.

A wire of commercial nickel of 0.26 mm. diameter also failed to show any change of resistance with currents up to 4.5 milliamperes, and was apparently unaltered in other respects.

#### Discussion.

The foregoing results confirm those obtained by previous observers in that, with progressing occlusion of hydrogen, the resistance of palladium increases steadily and reaches a constant value. With regard to the proportional increase at saturation the results are, however, extremely divergent. For, while Fischer found increases which varied only between 68 and 69%, and McElfresh obtained the value 67% for both of the wires which he studied, Knott's results run from 63 to 83%, and those here reported from 56.6 to 74.7%. The values found for small wires are undoubtedly too high, owing to the effect mentioned under (2) in the summary of resistance results above, and the circumstance that observations of the saturation resistance had necessarily to be made during momentary interruption of the charging current. Moreover, since it has been shown that the presence of small amounts of alloy-forming impurities exerts a marked influence upon the occlusion<sup>1</sup> of hydrogen by palladium, it is likely that differences of purity between the various wires account in great part for the discrepancies shown, and it may be seen from Table II that the smallest increases of resistance found in the present

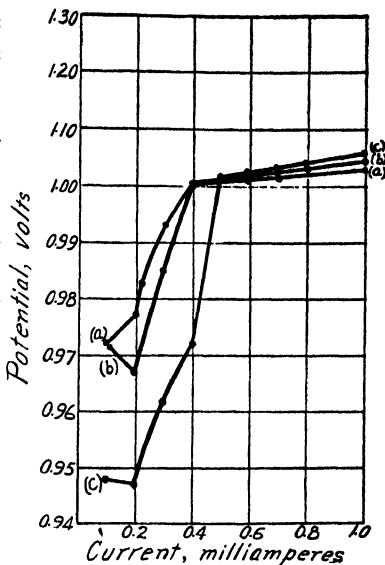


Fig. 6.—Potential of copper during electrolysis.

<sup>1</sup> Graham, *Proc. Roy. Soc. London*, 17, 500 (1869); Berry, *J. Chem. Soc.*, 99, 463 (1911); Sieverts, *Z. anorg. Chem.*, 92, 329 (1915).

investigation were obtained with the carefully purified metal, and the largest with that which was probably of poorest quality.

The possibility that the previous history of the palladium used affects its conduct in this matter, which is suggested by the well-known variability in the velocity and extent to which the metal occludes "molecular" hydrogen, should not be overlooked, but the results of these experiments show no indication of such an influence. Indeed, while observations upon this point were only incidental, the conduct of Wire No. 11 suggests rather that such an effect was absent. For this wire, which was of purified metal, and of sufficient diameter to be unaffected by the disturbing factors discussed in the next paragraph, gave reproducible results, the maximum resistance of 0.4080 ohm, which it maintained during two days of electrolysis on first being charged, being exactly recovered and maintained in each of the two subsequent chargings.

The principal new observation of the present experiments is to be found in the change of resistance with change of charging current, which has been noted under (2) and (3) in the summary of resistance results above, and which is further evidenced by a dependence of the saturation resistance upon the current, such as is illustrated by the following observations from Expt. 12: the resistance having become constant at 4.3560 ohms with a current of 0.2 milliamp., fell in the course of an hour and a half to 4.3120 ohms, when the current was increased to 0.8 milliamp., and again became constant. When the current, some eight hours later, was lowered to 0.3 milliamp., the resistance rose to 4.3440 ohms. This inverse response of resistance to current in a saturated wire was found invariably with the small wires and ribbon. It should be noted that, as may be seen clearly from the curves of Fig. 3, an increase of current produced an uninterrupted decline of resistance to a new constant value, while a decrease of current usually caused the resistance to pass through a maximum.

Two possible explanations of these effects suggest themselves. The first is that, during electrolysis, there is formed upon the wire a conducting layer of some product of electrolysis, and that the thickness or conductivity of this layer responds immediately to any change of current or impressed potential.

There are considerations, however, which appear to make this explanation untenable. In the first place, if one regards the change of resistance after interruption of the charging current in connection with the accompanying change of potential, it is evident from the curves exhibited in Fig. 4, which represent the changes of both quantities for successive interruptions with the same cathode, that while the character of the potential curve undergoes great modification between the first interruption and the last, the character of the resistance curve remains unaltered. If

the changes of resistance were indeed due to processes occurring in the portion of the electrolyte which immediately surrounds the wire, we should not expect their character to remain the same while the changes of potential suffered such radical alterations.

In the next place, the modification of the potential curves with successive interruptions is alone a sufficient indication of changes occurring in the wire, or in its surface, rather than in the electrolyte. For it is scarcely conceivable that persistent alterations could be produced in the electrolyte.

Finally, if the effect were due to changes in the electrolyte, a similar effect might be expected with copper cathodes, when subjected to the same treatment. Yet none was apparent, the potential of the copper varying regularly, and without the rise and subsequent fluctuations shown by that of palladium, while its resistance remained unaltered.

It seems necessary to conclude, therefore, that the change of resistance observed after interruption of the charging current is produced by changes in the cathode or its surface. It also appears that these changes are not confined to the immediate surface of the metal, which plays a part in determining the potential, for in that case we should again expect some parallel between the variations of potential and those of resistance.

If, then, the change of resistance after interruption of electrolysis is to be explained by processes occurring within the cathode, it is yet evident that these processes cannot be merely a continuation of those which have occurred during charging; for no matter how long or how often the wire has been charged to the attainment of steady resistance, a further increase of resistance takes place when the current ceases. The processes are also immediately responsive to any changes of current, and are evidently reversible.

As a tentative explanation, which agrees at least qualitatively with all of the facts observed, the following seems worthy of consideration. The steady rise of resistance observed during the progress of occlusion is due to combination of hydrogen with palladium to form an alloy of higher resistance than the pure metal. When, with steady current and applied voltage, this combination has come to equilibrium, the wire possesses the resistance of the saturated alloy, diminished by a conductance due to the uncombined hydrogen, or to some portion of the latter. Upon the interruption of the current, after this state has been reached, the gradual disappearance of the conducting hydrogen produces an increase of resistance, at first rapid, but diminishing in rate until a constant value has been attained. So long as the charging current continues without variation the loss of conducting hydrogen is made good by further occlusion, but any change of current causes either the rate of supply or the rate of loss to predominate, with corresponding loss or gain of resistance,

until a steady state has again established itself. This accords, evidently, with the fact that the lower the current at which the steady state sets in, the higher is the corresponding resistance.

On comparing the conduct, after the interruption of electrolysis, of wires of different sizes, shown in Fig. 2, it appears that the increase of resistance is greatly dependent, both as to magnitude and duration, upon the dimensions of the wire. With the 0.32 mm. wire, No. 11, the effect could not be found. In the 0.1 mm. wires, Nos. 5, 6 and 9, the increase was from 0.10 to 0.15 volt, and was complete in less than four hours, after which the resistance usually remained nearly constant for many hours. In the 0.05 mm. wire, No. 7, the increase amounted to almost 0.9 volt, and required some twenty-eight hours for its completion. With the ribbon of No. 12, however, which was 0.018 mm. thick, and in ratio of surface to volume was equivalent to a wire of 0.035 mm. diameter, the effect again fell to a very small magnitude. Since the form of the ribbon was much more favorable than even that of the smallest wire to rapid escape of hydrogen, it might be supposed that this process made its influence felt in the case of the ribbon before the rise of resistance had come to an end. But doubt is thrown upon this explanation of the behavior of the ribbon by the fact, also apparent from Fig. 2, that a decline of resistance began relatively early also in the large wire, No. 11, and in one of the 0.1 mm. wires, No. 9. Whatever the cause of the divergent conduct of the ribbon, it is at any rate evident that dimensions have a marked influence, and hence the process which is responsible for the rise of resistance must be supposed to take place chiefly near the surface.

If the effect is to be explained as due to conductance by the occluded hydrogen, it seems necessary, in view of this superficial character, to conclude further that the conducting hydrogen is of a form which exists only for a brief time and passes then into a nonconducting form, or one of relatively small conductivity, or else to suppose that a uniform distribution by diffusion had not been attained even in the numerous cases in which the resistance became constant within forty-eight hours, and remained so during days of continued electrolysis. For, unhindered diffusion assumed, a single form of uncombined hydrogen, if there were only one, must have been uniformly distributed through the wire when the steady state was attained, and the loss of conductance on interrupting the current would have been proportionally as great for thick wires as for those of smaller diameter. While there exist many grounds, from the work of other observers as well as from these experiments, for believing that the diffusion of hydrogen in palladium is sufficiently rapid to have insured uniform distribution in all of the experiments under discussion, the conclusion just indicated with regard to the condition of the occluded hydrogen is obviously in need of support by further experiments, and its

consequences need not be drawn at present. A particular reason for caution will be found below.

With regard to the observations upon the cathode potential, which have already been summarized, it should be pointed out that the indications as to the initial drop of potential are somewhat doubtful. For if, in any experiment, the electrode wire did not rest closely against the siphon tip of Fig. 1a, and in consequence an appreciable ohmic fall was included in the potentials observed before the interruption of electrolysis, the effect must have been to produce such an instantaneous drop upon the interruption of the current as that found, and the magnitude of this drop must have increased with the current, as was the case. Although inspection of the cell before and after each experiment showed the wire to be closely held, it is, therefore, not certain that the first, falling part of the potential curves of Fig. 4, to the point A, corresponds to any process directly related to occlusion. The second, more slowly falling portion of the curve, from A to the minimum, appears to be merely the usual decay of polarization after the cessation of electrolysis.

The recovery of potential, however, seems to warrant further study for its indications as to the diffusion of hydrogen from the interior. It varied greatly in character and magnitude, sometimes showing the regularity seen in Curve 1, Fig. 4, and in other instances consisting of a series of fluctuations, and is probably due to the cause to which Helmholtz<sup>1</sup> attributed irregularities which he observed in platinum cathodes, namely, the existence within the metal of regions of different hydrogen concentration. The explanation agrees qualitatively with many of the observations, such as an exceptionally large and rapid recovery found with the ribbon of Expt. 12, and a very small recovery for the 0.32 mm. wire, and the fact that the recovery seemed to be most regular when a constant current had been employed in charging. But diffusion at a constant rate does not seem to be alone adequate to account for several such observations as may be illustrated by the first interruption of Expt. 7. Here the applied voltage and the cathode potential had risen steadily during the previous electrolysis, and hence possessed, at the time of interruption, values higher than any which had gone before. Yet upon interruption the potential, after falling from 1.2180 volts to 0.4479 volt, or lower, rose in the course of nine hours to 0.4840 volt. Since it would seem that under the conditions mentioned, and with a constant coefficient of diffusion, the concentration of hydrogen at the time of interruption must either have diminished continuously from the electrode surface inward, or must have been uniform throughout the wire, it is not readily seen how a reversal in the course of the potential curve can be explained, unless it is supposed that owing either to local differences in the rate of

<sup>1</sup> *Pogg. Ann.*, 150, 494 (1873).

diffusion or to its variation with time, there existed at some depth within the wire concentrations higher than that obtaining immediately within the surface. The occurrence of the recovery in such cases is, therefore, not improbably related to the fact observed by Lessing<sup>1</sup> that the rate of diffusion of hydrogen through palladium declines for some time before becoming constant.

The gradual disappearance of the recovery with repeated interruptions, seen in Fig. 4, is most readily accounted for as due to slow equalization of hydrogen concentrations throughout the metal. If this is the correct interpretation, it can hardly be supposed that saturation had been reached in most of the experiments here recorded, for in the experiment of Fig. 4, which was that conducted with the thin ribbon, conditions were the most favorable to speedy saturation, and yet five repetitions of charging were required before the disappearance of the recovery. On the other hand, if saturation had not been reached in the other experiments, it is difficult to understand the constancy of resistance long maintained in many instances, and particularly the reproducibility of this constant resistance already pointed out in connection with Expt. 11. The reconciliation of these apparently discordant indications must await the completion of further experiments.

The uncertainties regarding the attainment of saturation evidently do not affect the observations upon the inverse response of resistance to charging current, and the probability that this is due to conductance by occluded hydrogen, although they have direct bearing upon the question of the form in which this hydrogen is present.

The results with copper and nickel wires seem to show that these metals occlude very little hydrogen, if any, under the conditions of these experiments, although both are known to occlude considerable amounts of "molecular" hydrogen at higher temperatures.

Since the experiments thus far described were all conducted in cells of one type, it seemed desirable to make observations under somewhat different conditions, particularly with regard to the distribution of current at the cathode.

A cell of half-liter volume was employed, in which the cathode wire was supported upon a stirrer which revolved at 100 r. p. m., so that each side of the cathode in turn was presented toward the anode. The platinum points upon the stirrer, to which the cathode was fused, connected with a Wheatstone bridge through mercury seals which served also to close the cell from the air. The resistance of the leads was eliminated by compensating until the original resistance read was that estimated for the palladium wire, so that the observations, while affected with a small constant error, are of high relative accuracy. The arrangements were otherwise

<sup>1</sup> *Verh. deutsch. physik. Gesell.*, 4, 569 (1906).



the same as those described above, except that provisions for the measurement of potential were omitted.

The electrolyte was 2 *N* sulfuric acid, prepared as before, and the wires studied were from an American source. They were about 11 cm. long and of 0.05 mm. diameter.

After charging with a steady current of 1.5 milliamp. until the resistance had become constant, electrolysis was interrupted and the observations were made of which the results are displayed in Fig. 7. Here Curve 1 is for a first interruption after 71 hours' charging of Wire No. 1, while the other curves refer to three successive interruptions with

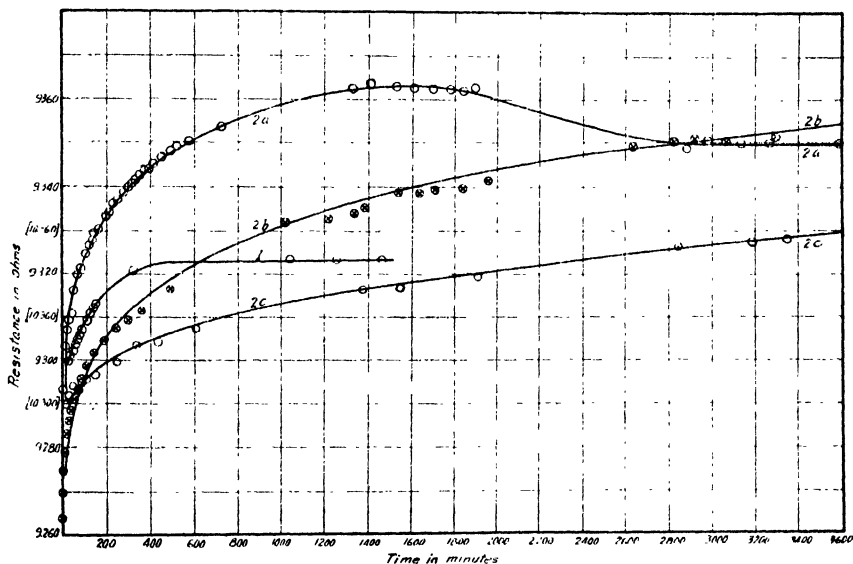


Fig. 7.

Wire No. 2, made after 68, 51 and 22 hours' charging. Curve 1, for which the ordinates are given in brackets, would extend above the figure if drawn to the same ordinates as the other three, to which the unbracketed numbers apply. The rise of resistance in No. 1 was, therefore, greater and much more rapid than any of those observed with No. 2.

The results dispose of the possibility that the supplementary rise of resistance after the interruption of electrolysis might have been due to the peculiar distribution of current at the cathode in the earlier experiments. The differences shown between the first interruptions, Nos. 1 and 2a, and between the successive interruptions of No. 2, are much greater than any previously found between wires of the same diameter. This is probably to be attributed to the fact that the preliminary annealing *in vacuo*, to which all of the earlier wires were subjected, was here omitted.

A study of these effects by another method has been undertaken.

### Summary.

1. Observations have been made of the changes in the electrical resistance and in the cathode potential of palladium wires, both during their occlusion of hydrogen electrolytically evolved, and after the interruption of electrolysis.

2. The proportional increase of resistance at apparent saturation has been found to vary widely, even with wires from the same lot of carefully purified palladium.

3. The resistance of saturated wire of 0.1 mm. diameter or less, observed during momentary interruptions of electrolysis, has been found to vary in a well-defined manner with the polarizing current; and the resistance after the interruption of electrolysis has been shown to undergo changes which are reversible and reproducible.

4. Saturated wire of 0.32 mm. diameter has been found not to exhibit these changes.

5. Considerations are given which make it probable that the changes of resistance in the smaller wires are due to processes occurring within the metal, and not far removed from its surface.

6. The tentative conclusion is suggested that hydrogen occluded at the cathode surface exists for some time in a transitional state in which it possesses an electrical conductance of its own, and passes gradually into another form which has much less conductance, or none.

7. Characteristic changes have been observed, after the interruption of electrolysis, in the cathode potential of saturated palladium wire, and certain connections have been noted between the manner and magnitude of these changes and the conditions of electrolysis.

8. A few observations have been made upon copper wires which show that this metal does not suffer any measurable alteration of electrical resistance, under the same conditions which produce a high degree of occlusion in the case of palladium.

9. A single experiment has been made upon nickel wire, which appears to show that it too is unable to occlude sufficient hydrogen, under the conditions of these experiments, to produce any perceptible alteration of its electrical resistance.

PRINCETON, N. J.

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## THE ACTION OF MAGNESIUM ON SOLUTIONS OF POTASSIUM CHLORIDE.

By FREDERICK H. GETMAN.

Received September 18, 1916.

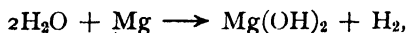
It has long been known that metallic magnesium reacts very slowly with distilled water at ordinary temperatures, the products of the reaction being magnesium hydroxide and hydrogen. An apparently similar, though more energetic, reaction has been shown to occur when magnesium

is introduced into an aqueous salt solution. On the other hand, when magnesium is introduced into a solution of one of the caustic alkalies no reaction takes place.

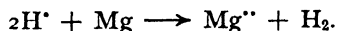
In an attempt to determine the difference of potential between metallic magnesium and various magnesium salts, the attention of the author was directed for the first time to the unusual reaction between magnesium and saline solutions. After reviewing the literature of the subject,<sup>1</sup> it became evident that none of the explanations of the phenomenon which have been advanced is wholly satisfactory. Undoubtedly the best explanation is that suggested by Kahlenberg based upon the assumption that solutions are chemical combinations of solvent and solute in varying proportions. While this assumption offers a ready explanation of all of the phenomena described and consequently is superior to the explanations advanced by earlier investigators in this field, it is open to the objection that it involves a step backward to the older theories of solutions. The modern theory of solutions has proven to be so comprehensive a generalization that it does not seem unreasonable to assume that it can be invoked to explain the action of metallic magnesium on saline solutions.

With this end in view, the present investigation was undertaken.

**Theoretical.**—The reaction between magnesium and water may be represented by the following equation:



or writing the reaction in terms of ions, we have



Since, for a definite temperature, the ionic product of water is constant,  $c_{\text{H}^+} \times c_{\text{OH}^-} = \text{const.}$ , it follows that the rate of the reaction should decrease owing to the increase in the concentration of hydroxyl ions furnished by the dissolved magnesium hydroxide. When the solubility product of magnesium hydroxide is exceeded, then the reaction should proceed at a uniform rate, provided that the effective surface of the metal is not reduced by the accumulation of precipitated magnesium hydroxide. In general, aqueous solutions react more energetically with magnesium than pure water alone. This suggests that the dissolved substance may function as a catalyst in the reaction. The possibility that the solute might function as a catalyst was suggested by Tommasi<sup>2</sup> in connection with his experiments on the action of magnesium on solutions of potassium chloride. In commenting on this suggestion, Kahlenberg<sup>2</sup> says: "It would scarcely be helpful to dismiss the matter by saying that in these

<sup>1</sup> Tommasi, *Bull. soc. chim.*, [3] 21, 885 (1899); Lemoine, *Compt. rend.*, 29, 291 (1899); Mouraour, *Ibid.*, 130, 140 (1900); Kahlenberg, *THIS JOURNAL*, 25, 380 (1902); Roberts and Brown, *Ibid.*, 25, 801 (1903).

<sup>2</sup> *Loc. cit.*

diverse solutions the rate of evolution of hydrogen is increased by the catalytic action of the solute when hydrogen is liberated more rapidly than from water, and that the rate is diminished by the negative catalytic action of the solute, when the formation of hydrogen takes place less rapidly than from water." As a matter of fact, Kahlenberg's experiments with a wide variety of solutes, failed to reveal but three cases where the rate of the reaction between magnesium and water was lessened. Glycerol, mannite and cane sugar each produced a distinct retardation of the reaction, but it is conceivable that this effect may be traceable to the presence of several hydroxyl groups in each of these compounds. Whatever the cause of the retarding action of these substances, the fact seems to be well established that dissolved substances, as a rule, tend to promote rather than to retard the reaction between magnesium and water. A further consequence of the catalytic theory is, that the dissolved substance should remain unaltered throughout the reaction and be recoverable in its original amount at the end of the reaction.

**Materials.**—The magnesium used in this investigation was obtained in the form of wire 3.3 mm. in diameter. Analysis showed it to contain 99.66% of magnesium, together with a residue consisting of aluminium and iron. Spectroscopic examination of the wire with a grating spectroscope confirmed the results of chemical analysis. The potassium chloride was obtained from a reliable source and, after recrystallization, was found to be of a high degree of purity. In addition to ordinary distilled water, so-called "conductance water" was used. This was prepared in the usual manner by successive redistillation of ordinary distilled water, first from chromic acid and then from alkaline potassium permanganate, the final distillate being condensed in block tin and stored in a receiver of Jena glass. The water obtained by this process was found to possess a specific conductance of about  $3 \times 10^{-6}$  reciprocal ohms.

### Experimental.

The present investigation is limited to the study of the action of metallic magnesium on aqueous solutions of a single solute, potassium chloride. The experimental work may be conveniently considered in the following order: (a) measurement of the volume of hydrogen obtained from water under varying conditions, (b) measurement of the volume of hydrogen obtained from solutions of potassium chloride of different concentrations, (c) determination of the difference of potential between magnesium and solutions of potassium chloride, (d) study of the concentration of the hydrogen ion in the presence of magnesium in both pure water and solutions of potassium chloride, and (e) determination of the concentration of potassium chloride in a solution before and after the action of magnesium.

(a) **Volume of Hydrogen from Water.**—A form of apparatus similar to that shown in Fig. 1 was used in measuring the volume of hydrogen

resulting from the action of metallic magnesium on water alone or on aqueous solutions of potassium chloride. It consisted of a graduated gas-measuring tube, B, of 50 cc. capacity and a leveling tube, A, the two tubes being connected by means of a piece of rubber tubing fitted with a pinchcock, E. In carrying out an experiment with this apparatus, E was closed and, after removing the rubber stopper and tubing at D, A was filled with water or with the solution to be studied. The pinchcock E was then opened and the liquid in A was allowed to flow out until any air bubbles which might be present in the tubing were removed. After again closing E, the tube B was filled full of the liquid to be studied, a piece of magnesium wire of known dimensions was dropped in, and the stopper D was quickly inserted, taking care to avoid the inclusion of air. On inverting the tube B, the piece of magnesium wire could be readily caused to fall into place at C, the end of the glass tubing projecting through the stopper serving to hold it in a vertical position as shown in the illustration. The pinchcock E was then opened and the tubes A and B clamped in such relative positions that the level of the liquid in the former was slightly higher than that in the latter. Readings of the volume of gas disengaged were made with the liquids in the two tubes at the same level. The pieces of magnesium wire used were exactly 50 mm. in length and were carefully polished in a lathe to an average diameter of 3.25 mm. before introducing into the liquid in the tube B. It was assumed that the effective surface

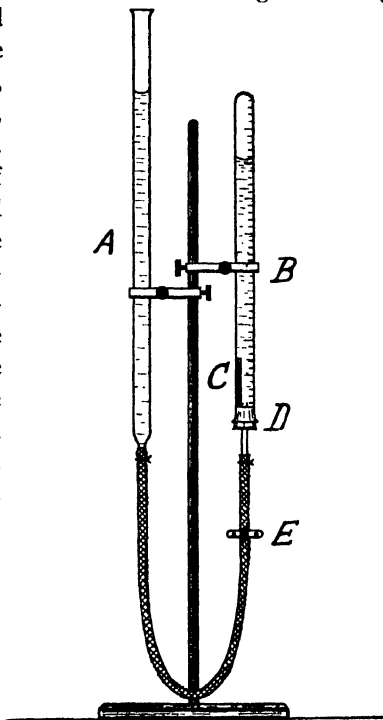


Fig. 1.

of the wire was its total superficial area minus the area of the end in contact with the rubber stopper. That this assumption was justifiable was proven by the fact that only a slight tarnish was observed on the ends of wires which had been immersed for several days. The effective surface of magnesium in each of the following experiments may thus be taken to be 518.9 sq. mm. In the subjoined tables,  $t$  denotes the interval of time in hours from the beginning of the experiment,  $v$  denotes the volume of gas evolved in cubic centimeters and reduced to  $0^{\circ}$  and 760 mm., and  $\Delta v / \Delta t$  gives the rate at which gas is evolved,  $\Delta t$  being reckoned from the initial time as zero.

TABLE I.  
Distilled Water.

<i>t.</i>	<i>v.</i>	$\Delta v/\Delta t.$
6	0.26	0.043
21	0.44	0.021
45	0.55	0.011
69	0.60	0.009
213	0.80	0.004
261	0.89	0.004
405	1.44	0.004
501	1.79	0.004

TABLE II.  
Conductance Water.

<i>t.</i>	<i>v.</i>	$\Delta v/\Delta t.$
48	0.35	0.007
120	0.54	0.005
360	1.37	0.004
384	1.48	0.004
408	1.59	0.004
432	1.68	0.004
624	2.57	0.004

TABLE III.  
Distilled Water Saturated  
with Air Freed from Carbon  
Dioxide.

<i>t.</i>	<i>v.</i>	$\Delta v/\Delta t.$
48	.15	0.024
72	.38	0.019
120	.59	0.013
168	.77	0.011
216	.86	0.009
240	.95	0.008
336	2.34	0.007
384	2.48	0.006

The water used in the first two experiments was freed from dissolved air, while that used in the last experiment was saturated with air from which the carbon dioxide had been removed by passing it successively through a solution of potassium hydroxide and a column of soda lime. The data recorded in Tables I and II indicates that magnesium reacts initially at nearly identical rates with ordinary distilled water and with that which has been freed from dissolved gases, and that ultimately the two rates become equal. On the other hand, the data of Table III shows that the presence of dissolved air augments the volume of hydrogen liberated in a given interval of time. The results obtained with distilled water confirm the results of Kahlenberg<sup>1</sup> and Bryant,<sup>2</sup> the latter of whom states that magnesium reacts equally well with both boiled and unboiled water. The experiments of Roberts and Brown,<sup>1</sup> however, led to the conclusion that magnesium is without action on distilled water, boiled free from dissolved gases, and cooled out of contact with air. A further deduction drawn by the last-mentioned authors from their experiments was that magnesium reacts with water which has been boiled and subsequently charged with oxygen. This conclusion is fully confirmed by the data recorded in Table III. From the evidence at hand, it seems justifiable to conclude that metallic magnesium reacts slowly with the purest distilled water and that the rate of reaction is augmented by the presence of neutral dissolved gases.

(b) **Volume of Hydrogen from Solutions of Potassium Chloride.**—In view of the fact that magnesium reacts at approximately the same rate with ordinary distilled water as with conductance water, the former was used in preparing the solutions of potassium chloride.

Two distinct series of experiments were carried out and the agreement between the results was as close as could be expected when the inherent defects of the method are taken into consideration. The solubility of the evolved hydrogen in the solution and the difficulty of removing the last

<sup>1</sup> *Loc. cit.*<sup>2</sup> Bryant, *Chem. News*, 80, 211 (1899).

adhering bubbles of gas from the surface of the magnesium wire constituted the chief defect in the method and introduced an appreciable error for which no correction was attempted. The curves shown in Fig. 2 are plotted from the experimental data, with the exception of that for  $N$  KCl, which is calculated from Kahlenberg's data, on the assumption that the amount of hydrogen evolved is proportional to the surface of magnesium exposed in the solution. The full line curves show the relation between time and the volume of hydrogen disengaged, while the dotted curves represent the variation in the rate of gas evolution with time. It will be observed that the rate of reaction between magnesium and water is greatly accelerated by the presence of potassium chloride. Furthermore, it is evident that the increase in gas evolution is not proportional to the increase in concentration of the solution. All of the curves show a tendency to become rectilinear with time, indicating that the reaction has attained a constant rate. None of the curves show the inflection which is characteristic of the curves of Roberts and Brown,<sup>1</sup> notwithstanding the fact that readings were taken every twenty minutes during the earlier stages of the reaction where this effect was observed. Direct comparisons with the data of the above investigators could not be made because of the insufficient information as to the dimensions of the magnesium used in their experiments.

(c) **Difference of Potential between Magnesium and Potassium Chloride Solutions.**—Determinations of the difference of potential between magnesium and solutions of several electrolytes were made by Kahlenberg.<sup>1</sup>

The measurements were made at  $20^{\circ}$  against the normal calomel electrode, the potential of which was assumed to be 0.56 volt. The following table summarizes the results obtained, the value of each difference of potential representing the mean of four determinations in which different bars of magnesium were used:

TABLE IV.		
Electrolyte.	Concentration.	Diff. of potential.
NaCl.....	2 (mols per liter)	1.163 (volts)
NaOH.....	1	1.111
KOH.....	1	1.140
KOH.....	0.1	1.105
MgSO <sub>4</sub> .....	1	1.366

It was observed that in the solution of sodium chloride, the e. m. f. changed but slightly with time; in the caustic alkali solutions the e. m. f. slowly diminished on standing, while in the solution of magnesium sulfate it showed a tendency to increase. In discussing these results, Kahlenberg says: "The difference of potential between magnesium and the solutions would be expected to be higher in the case of solutions that are vigor-

<sup>1</sup> *Loc. cit.*

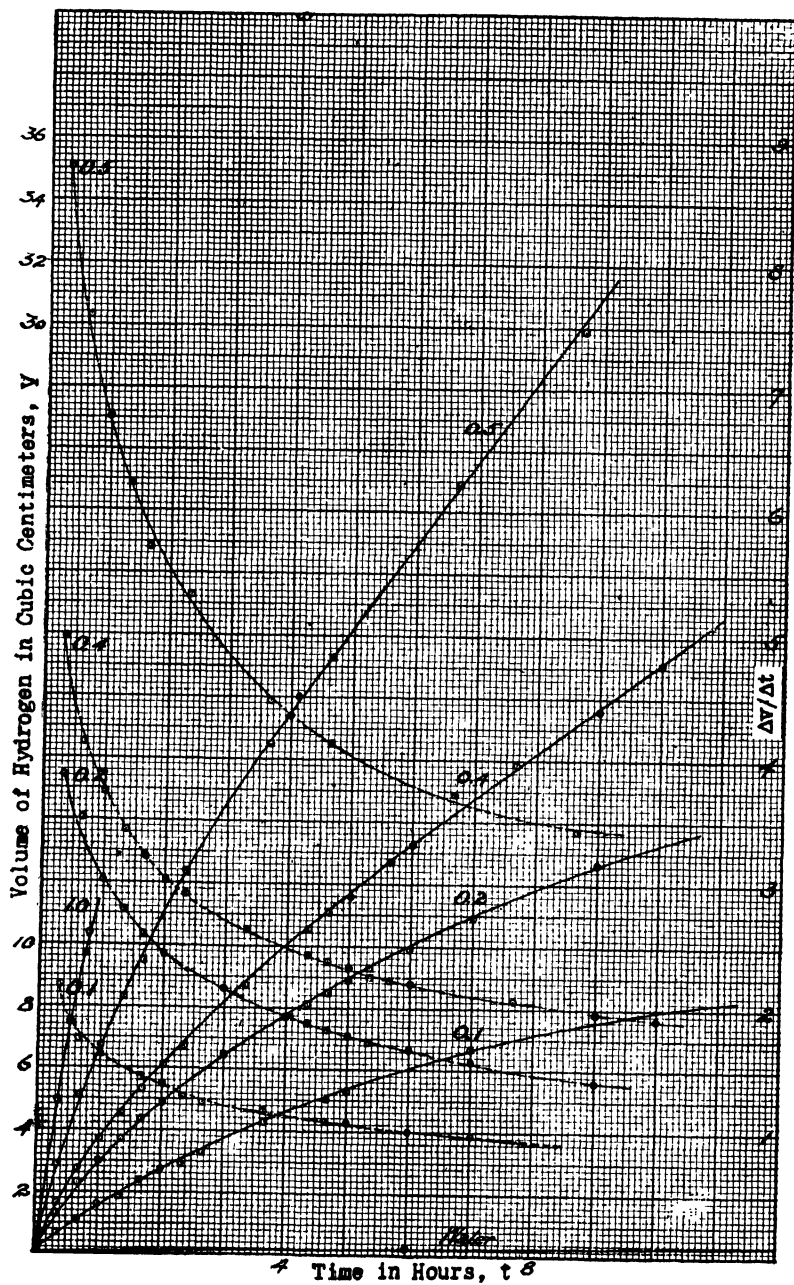
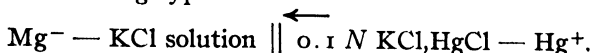


Fig. 2.



ously attacked than in solutions in which the action is slight. The experimental data are in accord with this." Similar determinations of differences of potential between magnesium and solutions of potassium chloride were made in the present investigation. The data given in this subjoined tables were obtained from measurements of the e. m. f. of cells of the following type:



the current flowing outside of the cell in the direction of the arrow. The cell was immersed in a thermostat maintained at  $25^\circ \text{C.} \pm 0.05^\circ$ , at which temperature the potential of the calomel electrode was taken to be 0.6186 volt. Two different magnesium electrodes were used in these experiments, care being taken to remove all traces of oxidation by polishing with emery cloth immediately before immersing in the solution. The results tabulated represent the mean of several determinations with each of the two electrodes:

TABLE V.—0.1 N KCl.

Time.	Diff. of potential
0 (min.)	1.1007 (volts)
10	1.0948
20	1.0920
30	1.0893
40	1.0868
50	1.0860
120	1.0840
250	1.0690
450	1.0638
1200	1.0589

TABLE VI.

Concentration.	Diff. of potential.
0.1 (mol. per liter)	1.0962 (volts)
0.05	1.0760
0.02	1.0517
0.01	1.0199
0.005	1.0069
0.001	0.9870
0.0005	0.9170
0.0001	0.8856

It will be seen from Table V that when magnesium is immersed in 0.1 N KCl, the difference of potential between the metal and the solution decreases with the time. This effect is undoubtedly caused by the gradual accumulation of the products of the reaction upon the surface of the electrode and a consequent lessening of its rate of solution. When the difference of potential is plotted against the time, a curve is obtained which is similar to that expressing the relation between the rate of evolution of hydrogen and the time as shown in Fig. 2. The values of the differences of potential given in Table VI are based upon measurements of electromotive force which were made as soon as possible after introducing the magnesium electrodes into the respective potassium chloride solutions. They may, for all practical purposes, be regarded as the differences of potential between an untarnished surface of magnesium and the different solutions of potassium chloride given in the table. As will be seen, the difference of potential decreases with decreasing concentration, a result which is not unexpected, when it is remembered that the rate of solution of magnesium is conditioned by the amount of salt present.

An interesting phenomenon was noted in connection with the study of the electromotive behavior of magnesium in solutions of potassium chloride. When the surface of the electrode was cleaned by immersion in acid, it was found that the difference of potential between it and the solution was invariably lower than when the surface was cleaned by means of emery cloth. The influence of the preliminary treatment on the subsequent behavior of the electrode is clearly shown by the data of Table VII.

TABLE VII.—0.1 *N* KCl.

Electrode.	Potential after treatment with		Difference.
	Emery.	Acid.	
I.....	1.0957	1.0666	0.0291
I.....	1.0958	1.0423	0.0535
II.....	1.0935	1.0524	0.0411
II.....	1.1000	1.0530	0.0470

While the value of the difference of potential established between a freshly polished magnesium electrode and 0.1 *N* KCl was practically constant and reproducible, the corresponding values obtained with electrodes previously immersed in acid were always numerically smaller and varied considerably. It will be observed that the differences of potential established by electrodes which have been treated with acids are comparable with the final values of Table V. This tends to confirm the suspicion that the surface of an electrode which has been immersed in acid is enveloped by an adsorbed film of hydrogen which cannot be removed by prolonged washing.

(*d*) **Concentration of the Hydrogen Ion.**—Attention has already been called to the fact that when magnesium is immersed in water, or in a solution of potassium chloride, an alkaline reaction ensues almost immediately. It is evident that any satisfactory explanation in this reaction must take into account the changes which occur in the concentration of the hydrogen ion as the reaction proceeds. With this end in view, determinations of the concentration of the hydrogen ion were made at definite intervals of time in reacting mixtures of water and magnesium and of potassium chloride solutions and magnesium. A hydrogen electrode consisting of a strip of platinum foil coated with platinum black and saturated with hydrogen under a definite pressure was used to determine the concentration of the hydrogen ion. When such an electrode is immersed in a solution which is normal with respect to the hydrogen ion, and is connected with a similar electrode, immersed in a solution of unknown hydrogen-ion concentration, *c*, the resulting e. m. f., *E*, can be calculated by means of the well-known formula of Nernst, *viz.*,

$$E = RT/nF \log_e 1/c.$$

Since it is more convenient to use the calomel electrode than the normal hydrogen electrode, the above expression may be written

$$E = RT/nF \log_e 1/c + \delta,$$

where  $\delta$  denotes the difference between the potential of the normal hydrogen electrode and that of the calomel electrode.

At a temperature of  $25^\circ$ , using a calomel electrode containing 0.1  $N$   $\text{KCl}$ , the formula becomes, on transforming to Briggsian logarithms,

$$E = 0.0595 \log 1/c + 0.33,$$

the value of  $\delta$  being 0.33 volt under these conditions.

A hydrogen electrode similar to that described by Hildebrand<sup>1</sup> was prepared and was found to attain equilibrium quickly and also to be both constant and reproducible. The hydrogen used was prepared by the action of granulated zinc on hydrochloric acid, and was washed by passing successively through solutions of potassium hydroxide and potassium permanganate. As in the foregoing experiments, the magnesium used was in the form of wire polished to an average diameter of 3.15 mm. and cut in 40 mm. lengths, thus giving a total surface of 411.6 sq. mm. Owing to the fact that in these experiments the solution was stirred before taking each reading, it may be assumed that the entire surface of the wire represents the effective surface. An enclosed type of Lippmann electrometer, sensitive to 0.0001 volt, was employed to determine the point of balance on the bridge wire, according to the familiar method of Poggendorff. Before beginning a series of measurements, care was taken to insure the complete saturation of the hydrogen electrode at atmospheric pressure. By passing a current of hydrogen through the electrode at such a rate that about one bubble per second escaped from the immersed end of the electrode, it was found that complete saturation could be secured in ten minutes, and that by continuing the passage of gas at the same rate, the constancy of the electrode could be maintained indefinitely. The volume of water or of solution used in all of the experiments was 25 cc. and care was taken not to immerse the hydrogen electrode to a greater depth than was necessary to prevent the free escape of hydrogen. Having secured a completely saturated electrode, connection with the calomel electrode was established by dipping the siphon tube of the latter into the contents of the beaker. Having measured the e. m. f. of the combination as quickly as possible, the freshly polished magnesium wire was introduced and, after an interval of five or ten minutes, the e. m. f. was again determined. As soon as the point of balance on the bridge wire was obtained, connection with calomel electrode was broken by closing the stopcock in the siphon tube and then removing the latter from the

<sup>1</sup> Hildebrand and Harned, *Eighth Intern. Congr. Appl. Chem.*, 1, 217; *THIS JOURNAL*, 35, 847 (1913).

solution in the beaker. This procedure minimizes errors due to diffusion at the liquid junction. No attempt was made to introduce a correction for liquid potentials since such a correction would in every case be negligible in comparison with the experimental error. The solution in the siphon tube of the calomel electrode was renewed before the beginning of each experiment, thus insuring a connecting solution which was strictly 0.1 *N* with respect to potassium chloride. The experimental data are

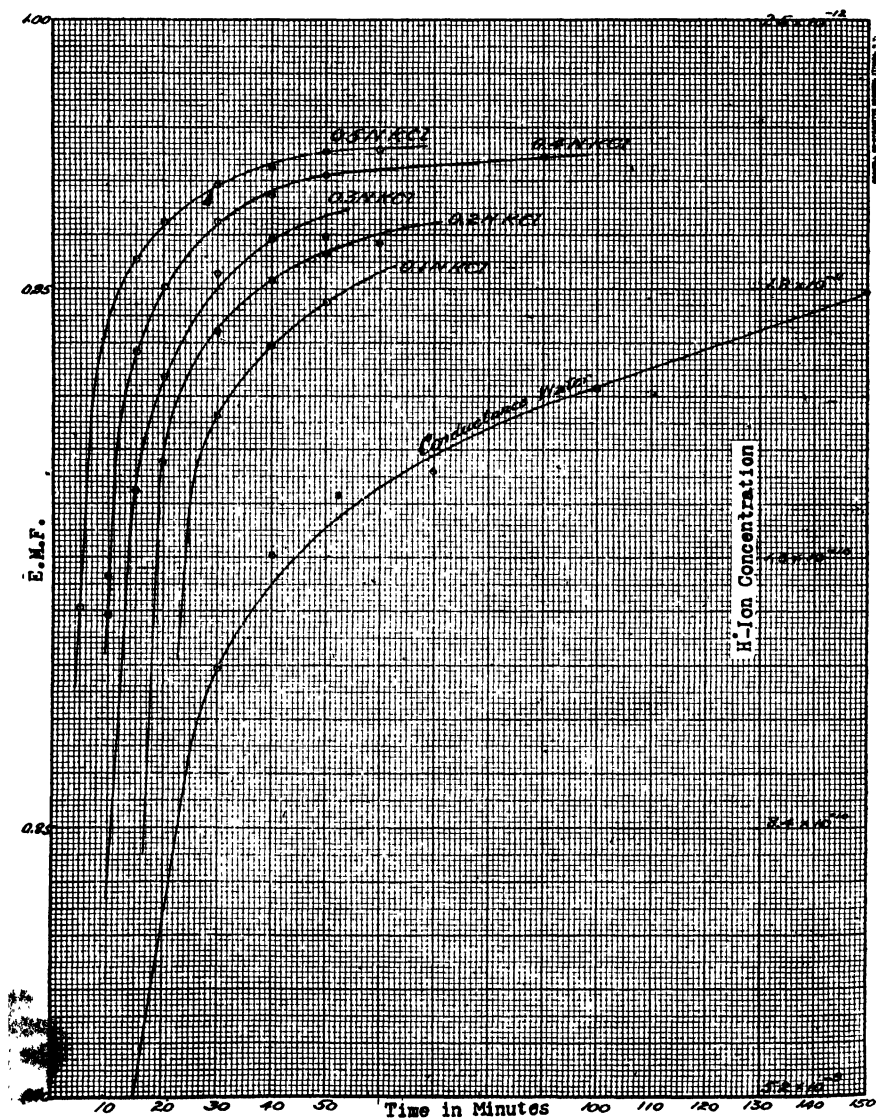


Fig. 3.

represented by the curves shown in Fig. 3. The influence of increasing amounts of potassium chloride in accelerating the reaction between magnesium and water with a consequent diminution of the hydrogen-ion concentration, is clearly shown. The rapidity with which the e. m. f. changes in the early stages of the reaction rendered it extremely difficult to secure satisfactory readings during the first five or ten minutes of an experiment. It will be observed that the curves of Fig. 3 all show a tendency to become horizontal with increasing time and that this tendency becomes more pronounced as the amount of potassium chloride is increased. This result furnishes weighty evidence in favor of the proposed explanation of the reaction between magnesium and water and the function of potassium chloride therein. According to this explanation, magnesium is assumed to dissolve in water by virtue of its high solution pressure, forming magnesium hydroxide. This latter substance undergoes ionization, thereby increasing the concentration of hydroxyl ions in the water and causing a corresponding decrease in the concentration of the hydrogen ions. The process will continue until the water becomes saturated with magnesium hydroxide, after which the concentrations of the hydroxyl and hydrogen ions will remain constant. The addition of increasing amounts of potassium chloride should not only accelerate the velocity of the reaction but also should increase the solubility of the magnesium hydroxide formed, with a consequent further depression of the limiting concentration of the hydrogen ion.

(e) **Concentration of Potassium Chloride before and after Reaction.**—

If the action of potassium chloride in the reaction between magnesium and water is purely catalytic, its amount should remain unaltered. As has already been stated, Tommasi<sup>1</sup> found this to be the case in his investigation of the action of magnesium on solutions of potassium chloride and, as a result, he suggested that the potassium chloride should be considered as a catalyst promoting the reaction between magnesium and water. With a view to verifying the statement of Tommasi that the initial weight of potassium chloride remains unchanged throughout the reaction, the following experiment was performed. A piece of freshly polished magnesium wire was immersed in distilled water containing a known weight of potassium chloride. The reaction was allowed to proceed for several days until the rate of evolution of hydrogen became very slow. Then, after scraping off the accumulated magnesium hydroxide from the wire as completely as possible, the entire reaction mixture was filtered and the wire and residue washed repeatedly with boiling water. The object of this last operation was to remove the last traces of adhering potassium chloride from the wire and the residual magnesium hydroxide. The filtrate was then treated with a solution of barium

<sup>1</sup> *Loc. cit.*

hydroxide and the precipitated magnesium hydroxide was removed by filtration. The excess of barium was next removed by means of a solution of ammonium carbonate and the resulting filtrate carefully evaporated to dryness. After freeing the residue from ammonium salts by cautious heating, it was raised to the temperature of a full Bunsen burner for twenty minutes. The weight of the ignited residue was then determined, after allowing it to cool in a desiccator. The amount of potassium chloride present initially was 0.1868 g. while the weight of the residue at the conclusion of the experiment was 0.1886 g. While it may be conceded that the experiment established the fact that there is negligible adsorption of potassium chloride by the surface of the magnesium wire and the magnesium hydroxide produced by the reaction, it is evident that the various steps involved in the recovery of the salt would in all probability bring about the decomposition of any compound which it might have formed with the products of the reaction. So far as the writer is aware, however, no compounds of potassium chloride and magnesium hydroxide are known.

**Discussion of Results.**—The proposed explanation of the reaction between magnesium and water and of the role of potassium chloride in accelerating this reaction has been confirmed by several distinct lines of experimentation of which perhaps the most satisfactory is that involving the determination of the change in concentration of the hydrogen ion as the reaction progressed. The function of potassium chloride in the reaction may be likened to other well-established cases of so-called "salt-action." For example, Ostwald<sup>1</sup> showed that when a 0.4 *N* solution of potassium nitrate was added to a solution of cane sugar containing a 0.05 *N* solution of nitric acid, the coefficient of velocity of inversion of the sugar was raised from 29.9 to 33.9. From this and similar experiments he was led to the conclusion that while the presence of a neutral salt containing an ion in common with the inverting acid lowers the concentration of the hydrogen ions of the latter, it also exerts a marked stimulating influence on the remaining hydrogen ions. Quite another type of salt action is that described by Van Name and Edgar.<sup>2</sup> They showed that the rate of solution of a number of different metals in aqueous solutions of iodine is greatly increased by the presence of potassium iodide. In the Silliman lectures delivered at Yale University in 1911 by Arrhenius,<sup>3</sup> he says: "It has been proved that salts exert a certain influence which is sometimes very great, especially on the velocity of reaction." While in the present investigation the influence of only one salt on the reaction has been studied,

<sup>1</sup> Ostwald, *J. prakt. Chem.*, [2] 31, 307 (1885).

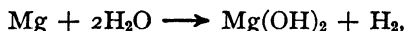
<sup>2</sup> Van Name and Edgar, *Am. J. Sci.*, [4] 237 (1910).

<sup>3</sup> "Theories of Solutions," p. 165, Yale Univ. Press, 1912.

it is believed that the explanation here given is of general application and that it is not necessary to invoke the assistance of the older chemical compound theory of solution.

### Summary.

In this paper the action of magnesium on solutions of potassium chloride has been investigated. The experimental work has involved (a) the measurement of the volume of hydrogen obtained by the action of magnesium on water prepared in a variety of ways, (b) the measurement of the volume of hydrogen obtained from solutions of potassium chloride of different concentrations, (c) the determination of the differences of potential between magnesium and solutions of potassium chloride, (d) the determination of the concentration of the hydrogen ion in both pure water and solutions of potassium chloride, and (e) the determination of the concentration of potassium chloride in a solution before and after the action of magnesium. The evidence furnished by these several lines of experimentation has led to the conclusion that the reaction between magnesium and water may be represented by the equation



and that the presence of the dissolved salt merely accelerates the reaction catalytically.

HILLSIDE LABORATORY, STAMFORD, CONN.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF PITTSBURGH.]

## OXIDATION-REDUCTION REACTIONS WITHOUT THE ADDITION OF ACID.

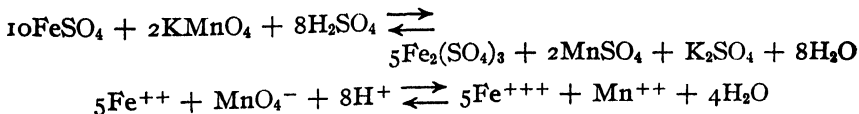
### III. FERROUS CHLORIDE AND POTASSIUM PERMANGANATE.

#### A New Method for the Preparation of Colloidal Hydrous Ferric Oxide.

BY MARKS NEIDLE AND JOHN N. CROMBIE.

Received October 6, 1916.

The most familiar reaction involving the oxidation of ferrous ion by permanganate ion, is that between potassium permanganate and ferrous sulfate in the presence of an excess of sulfuric acid, and may be formulated by either of the following equations:



The data necessary for predicting whether a mixture of aqueous solutions of ferrous chloride and potassium permanganate contains a sufficient concentration of hydrogen ion to render the normal reaction possible, and to make it go practically to completion are not available. Nor was it possible to gain this information from the results of the oxidation-

reduction reactions<sup>1</sup> already studied, for, in the latter, potassium dichromate was employed, which gives a concentration of hydrogen ion greater than that given by equivalent solutions of ferrous chloride or potassium permanganate. From our knowledge that hydrated manganese dioxide is formed when permanganate reacts with certain substances, *e. g.*, sugar, oxalic acid, manganese sulfate, in neutral or slightly alkaline solution (and even in weakly acid solution),<sup>2</sup> we might expect a similar result in the reaction with ferrous chloride or ferrous sulfate, without the addition of acid. A few preliminary experiments, however, pointed to the contrary, indicating that the ionic equation for the reaction between ferrous chloride and potassium permanganate, without the addition of acid, is the same as that in which an excess of acid is added. Then, it was possible to predict that one of the products is colloidal hydrous ferric oxide, while in the corresponding reaction with ferrous sulfate, the colloid is precipitated.

**Stoichiometric Relations.**—Ferrous chloride solutions, approximately normal, half-normal, fifth-normal and tenth-normal, were prepared by dissolving the commercial C. P. salt in the proper amounts of water, and filtering off the insoluble residue. These solutions were titrated by potassium permanganate of approximately the same normalities: first, with the addition of an excess of acid, and second, without the addition of acid.

Twenty-five cubic centimeters of ferrous chloride solution were taken in all titrations. In those with acid, 10 cc. of concentrated hydrochloric acid, 50 cc. of preventative solution, and water to make a volume of 400 cc. were added to the ferrous chloride and the titration conducted in the usual way, *i. e.*, until the first appearance of pink throughout the solution.

In the titrations without the addition of acid, the permanganate was immediately run into the ferrous chloride contained in a beaker. The first few drops produced a light yellow color, which gradually changed to a clear deep brown as more permanganate was added. Potassium ferricyanide was used as an outside indicator, and the end point was considered reached when a brown color was obtained, which did not turn green on standing for a few minutes. With a little practice, the end points were easily detected with a fair degree of precision. The titrations with the normal solution, however, presented a little more difficulty than the others, because of the intense brownish red color produced as the permanganate was added to the ferrous chloride.

It will be seen from the results, given in Table I, that the volume of permanganate required in a titration depends upon the manner of its addition. This was evidently due to the collateral reaction between

\* Neidle and Witt, *THIS JOURNAL*, 37, 2360-68; 38, 47-52.

<sup>2</sup> C. W. R. Powell, *J. Proc. Roy. Soc., New S. Wales*, 48, II, 223-41 (1914).



the permanganate and the chloride ion. We therefore decided to run similar titrations, using ferrous sulfate instead of ferrous chloride.

TABLE I.

Normality (approximate).	FeCl. Cc.	Titrations with acid. KMnO <sub>4</sub> . Cc.	Titrations without addition of acid.	
			Nearly sufficient KMnO <sub>4</sub> added all at once, stirred, and titrated to completion. KMnO <sub>4</sub> . Cc.	KMnO <sub>4</sub> added 1 cc. at a time and stirred vigorously after each addition. KMnO <sub>4</sub> . Cc.
0.1	25.00	26.13	29.27	27.66
		26.15	29.25	27.61
0.2	25.00	25.12	26.82	25.34
		25.11	26.83	25.40
0.5	25.00	24.00	25.12	23.97
		23.97	25.12	23.99
1.0	25.00	25.54	25.74	25.56
		25.52	.....	.....

**Titration of Ferrous Sulfate by Potassium Permanganate with and without the Addition of Acid.**—The procedure was identical with that followed in the ferrous chloride titrations, except that in those with acid, 5 cc. of concentrated sulfuric acid were substituted for the hydrochloric acid, and no preventative solution was employed. The ferrous sulfate solutions, in the titrations without acid, at first behaved exactly like those of ferrous chloride, but later gave a precipitate as indicated in Table II.

TABLE II.

Normality (approximate).	FeSO <sub>4</sub> . Cc.	Titrations with acid. KMnO <sub>4</sub> . Cc.	Titrations without addition of acid.	
			KMnO <sub>4</sub> . Cc.	Remarks.
0.1	25.00	24.88	24.90	Decided turbidity appeared when 15 cc. KMnO <sub>4</sub> were added. Precipitate settled gradually on standing.
		24.80	24.80	
0.2	25.00	22.97	22.95	Solution became cloudy when end point was nearly reached, and on standing a short time after completion of titration, a brown gelatinous precipitate formed.
		23.00	22.97	
0.5	25.00	25.63	25.60	Cloudiness did not appear until a short time after the completion of titration. Turbidity gradually increased and a precipitate finally formed.
		25.67	25.63	

**Discussion of Results.**—Since the ferrous sulfate titrations gave the same results (Table II, Columns 3 and 4), whether acid was used or not, we may conclude that the stoichiometric relations in the reaction between ferrous ion and permanganate ion are the same with and without the addition of acid. We may also conclude that, even in 0.1 *N* concentrations, ferrous sulfate and potassium permanganate react practically instantaneously.

The results of the ferrous chloride titrations, without acid, show the

same variations as found by Birch<sup>1</sup> and Friend<sup>2</sup> in their studies on the action of permanganate on ferrous salts in presence of hydrochloric acid. Birch attributes the larger amounts of permanganate to the loss of elementary chlorine. He also observes that "the results are, if anything, slightly better in concentrated than in dilute solution." This is also the case in the ferrous chloride reaction, without acid, as is seen from Column 5, Table I. Our data thus show that the greater the concentrations of the solutions, the less does the chloride ion interfere with the titrations. This may be explained by the greater speed of reaction between elementary chlorine formed in the side reaction and ferrous ion at the higher concentrations, and the consequent smaller proportionate loss of elementary chlorine.

The latter will also explain why the discrepancy in the results, due to the difference in the manner of adding the permanganate, decreases with increasing concentration. Friend has observed that the results in titrating ferrous salts by permanganate in the presence of hydrochloric acid are high when the permanganate is added rapidly, and more nearly theoretical when it is added slowly. He ascribes this discrepancy to the formation of an intermediate perchloride of manganese. We are inclined to attribute it to the presence of large local excesses of permanganate in the rapid titrations, resulting in considerable oxidation of chloride ion and loss of elementary chlorine.

The products in the ferrous sulfate-permanganate reaction are potassium sulfate, manganese sulfate, ferric sulfate and colloidal hydrous ferric oxide. Ferric sulfate, or rather the ferric ion, protects the colloid while the other salts are good colloid precipitants. A definite concentration of ferric ion is necessary to protect the colloid against precipitation by the sulfate ion. The amount of ferric ion in a ferric sulfate solution gradually diminishes because of hydrolysis.<sup>3</sup> Furthermore, colloidal hydrous ferric oxide accelerates the hydrolysis of ferric salts.<sup>4</sup> These considerations immediately furnish an explanation of the gradual appearance of a turbidity and ultimate precipitation in the ferrous sulfate-permanganate titrations without acid.

#### Products of the Ferrous Chloride-Potassium Permanganate Reaction.

—An amount of commercial C. P. ferrous chloride, containing an equivalent weight of ferrous iron, was dissolved in about a liter of water and filtered. An equivalent weight of permanganate ( $\frac{1}{5}\text{KMnO}_4$ ) was dissolved in about 600 cc. of water, and the resulting solution added in small portions—to avoid oxidation of chloride ion—to the ferrous chloride solution which

<sup>1</sup> *Chem. News*, 99, 61, 73 (1909).

<sup>2</sup> *J. Chem. Soc.*, 95, 1218 (1909).

<sup>3</sup> Schneider, *Ann.*, 257, 362 (1890).

<sup>4</sup> Goodwin and Grover, *Phys. Rev.*, 11, 193 (1900).

was shaken vigorously during the addition. Considerable heat was generated by the reaction, which yielded a perfectly clear, deep, brownish red solution. This solution, diluted to two liters, will be referred to as the "reaction mixture."

The reaction mixture became turbid after several weeks. The turbidity gradually increased, until, after nearly five months, two layers formed, the upper one being a perfectly clear yellow solution, and the lower one a brown ochery suspension, which could not be filtered off but did separate out on centrifuging for many hours. Boiling the original mixture gave a brown gelatinous precipitate, which was filterable. This precipitate readily dissolved in water to a solution, which was perfectly clear red by transmitted light, and turbid by reflected light, and from which the colloid could not be separated by centrifuging for many hours at about 2000 revolutions per minute.

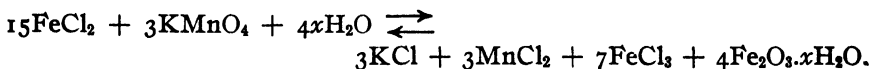
**Dialysis.**—Immediately after its preparation, 400 cc. of the reaction mixture were introduced into a parchment paper membrane and dialyzed with intermittent changing of the diffusate. The dialysis was continued for thirty-five days, and the perfectly clear reddish brown colloidal solution, which now suffered no change on boiling, was analyzed for iron, manganese, potassium and chlorine. The manganese and potassium were barely detectable, and therefore were not determined. The ratio of iron to chlorine in gram equivalents ( $\frac{1}{3}$  Fe, 1 Cl) was 26.3, and the colloidal solution contained 68.4% of the iron in the original mixture. We have thus obtained the common hydrosol of hydrous ferric oxide, protected, as usual, by a small amount of hydrochloric acid.

The percentage of the total iron in the mixture, obtainable in the form of the hydrosol, depends on the nature of the membrane and the method of dialysis. By continuous dialysis in the cold, using a parchment paper membrane, 82.1% of the total iron remained in the colloidal solution. The equation for the reaction points to only 53.3% of iron in the form of the hydrous oxide. The additional 15.1% obtained in intermittent dialysis and 28.8% in continuous dialysis, is due to hydrolysis of the ferric chloride. It has been mentioned that the reaction mixture gradually becomes turbid, and finally separates into two layers. Until the latter stage is reached, dialysis will readily yield a perfectly clear colloidal solution. After that, the colloidal solution obtainable by mixing the two layers and dialyzing, is slightly turbid in reflected light, though perfectly clear in transmitted light.

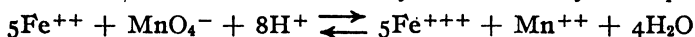
**Addition of an Excess of Permanganate to Ferrous Chloride.**—A slight excess of permanganate has no apparent effect other than a slight change in color, and, on dialysis, it rapidly diffuses through the membrane, leaving a clear hydrosol. A large excess does not cause an immediate change, but an odor of chlorine is observed, and the entire solution gels—within

an hour for 0.5 *N* solutions, and after several days for 0.1 *N* solutions. When such solutions have gelled, dialysis will not yield a hydrosol.

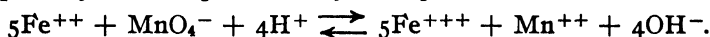
**Discussion of Results.**—Since all the manganese and potassium in the reaction mixture diffuse through the dialysis membrane, it may be concluded that they are present in the mixture as chlorides. Hence the products of the reaction are the chlorides of potassium, manganese and ferric iron, and colloidal hydrous ferric oxide. The reaction may now be written,



The ionic reaction, with acid, is usually formulated by the equation

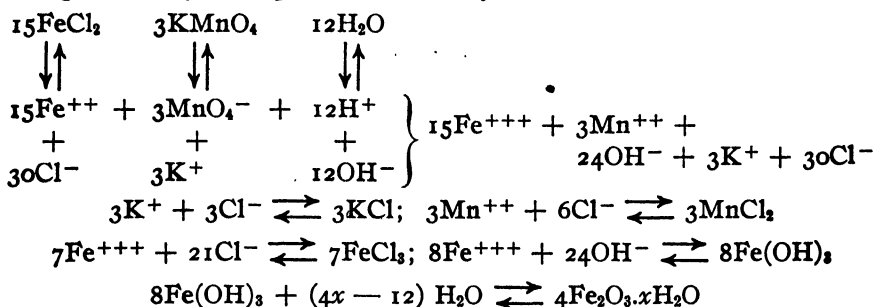


but is possibly better represented by the equation



If the concentration of hydrogen ion is very high, due to the presence of a strong acid, the concentration of hydroxyl ion will be kept at an exceedingly low value, as required by the ionic product constant for water. When no acid is employed, our results show that sufficient hydrogen ion for the reaction is furnished by the dissociation of the water, and by the hydrolysis of the ferrous chloride and potassium permanganate. But here hydroxyl ion accumulates, and soon the solubility product constant of ferric hydroxide is exceeded, when colloidal hydrous ferric oxide is formed.

The complete reaction between ferrous chloride and potassium permanganate may be represented ionically as follows:



The turbidity which appears in the reaction mixture, gradually in the cold and rapidly in the hot, is due to the hydrolysis of the ferric chloride. The ferric chloride, or rather the ferric ion, protects the colloid against precipitation by the manganese and potassium chlorides. Hydrolysis of the ferric chloride decreases the concentration of ferric ion, and, when it is reduced below the value necessary for protection, the colloid coagulates. This coagulation is, however, reversible, for the turbid reaction

mixture, on dialysis, will yield a practically clear sol. The reversibility in this case is due to the greater diffusion velocities of manganese and potassium chlorides as compared with ferric chloride. As the manganese and potassium chlorides diffuse, the residual ferric ion peptizes the coagulated colloid, and the sol is again formed.

### Summary.

The stoichiometric relations in the permanganate-ferrous sulfate and permanganate-ferrous chloride reactions are the same with or without the addition of acid. In the permanganate-ferrous chloride reaction, the collateral oxidation of chloride ion is practically avoided by adding the permanganate gradually and with vigorous stirring.

The products of the permanganate-ferrous chloride reaction are the chlorides of potassium, manganese and ferric iron, and colloidal hydrous ferric oxide, while in the permanganate-ferrous sulfate reaction, the corresponding sulfates are formed, and also hydrous ferric oxide, which is precipitated by the sulfate ion.

A gram equivalent of permanganate, dissolved in about 600 cc. water, was slowly added to a gram equivalent of ferrous chloride, dissolved in about a liter of water, and the resulting clear, deep brownish red solution diluted to two liters. This solution remained perfectly clear for several weeks, then gradually became more and more turbid, until finally a suspension settled out. Until the latter stage is reached, dialysis yields a perfectly clear brownish red hydrosol of hydrous ferric oxide. After a suspension settles out, dialysis will give a hydrous ferric oxide hydrosol which is slightly turbid in reflective light, but perfectly clear in transmitted light.

PITTSBURGH, PA.

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[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY OF HARVARD UNIVERSITY.]

## FURTHER STUDY OF THE ATOMIC WEIGHT OF LEAD OF RADIOACTIVE ORIGIN.

By THEODORE W. RICHARDS AND CHARLES WADSWORTH, 3D.

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The recent independent and almost simultaneous investigations upon the atomic weights of lead from radioactive minerals have proved with very little room for doubt that the substance derived from this source has a much lower atomic weight than ordinary lead.<sup>1</sup> This conclusion is so important in its theoretical relations that its every aspect should be carefully investigated. Accordingly, the present paper represents further

<sup>1</sup> Richards and Lambert, *THIS JOURNAL*, 36, 1329 (1914); Hönigschmid and St. Horovitz, *Compt. rend.*, 158, 1798 (1914); M. Curie, *Ibid.*, 158, 1676 (1914); Soddy and Hyman, *J. Chem. Soc.*, 105, 1402 (1914); also especially, Hönigschmid, *Sitzb. h. Akad. Wiss., Wien, IIa*, 123, 1 (Dec., 1914).

research in this direction, embodying determinations of the atomic weight of new samples of varied origin. The outcome entirely supports the earlier conclusion.

Four samples from widely separated sources were studied in the present research, namely, radio-lead from Australian carnotite, from American carnotite, from Norwegian cleveite, and Norwegian bröggerite.

The first of these samples was obtained in large quantity from the Olary mines of South Australia, through the kindness of Mr. S. Radcliff and Mr. E. R. Bubb, of the Radium Hill Company, of Sydney, New South Wales. The carnotite, an impure vanadate of uranium and potassium, mixed with much ilmenite and mica, was crushed and fused with excess of salt cake. The powdered product was extracted with cold water in agitators, dissolving the uranium and rare earths and leaving a suspension of barium, radium and lead sulfates, which was allowed to settle in lead-lined vats. After digestion with sulfuric acid to remove the iron, the separated sulfates were converted into carbonates by boiling with 20% sodium carbonate solution. The carbonates were dissolved in hydrochloric acid and the metals were reprecipitated as sulfates, which, after washing, were fused with sodium carbonate in graphite crucibles. Two kilograms of metallic lead thus reduced served as the basis of one of our present samples, as well as of the work now being continued in this laboratory.

The preliminary purification above described was carried out in Australia.<sup>1</sup> Our subsequent work with the sample is briefly described in a recent paper on the density of radio-lead,<sup>2</sup> but because so much depended upon the purification of materials in work of the sort under consideration, further details are desirable. Three different purified samples derived from the Australia lead were prepared as follows: In each case the metallic lead was dissolved in nitric acid, leaving practically no residue. Two portions of the nitrate thus obtained were taken; the first for the preparation of Samples A and B, and the second for the preparation of Sample C.

The first portion was precipitated with 20% hydrochloric acid from dilute solution, the precipitate being separated from the mother liquor by suction and dissolved in pure warm water to which enough acid had been added to prevent precipitation of the basic salt. Lead sulfide was precipitated from this solution by thoroughly scrubbed hydrogen sulfide gas, and after separation and washing was dissolved in pure nitric acid. The small portion oxidized to sulfate during this latter process was boiled with sodium carbonate for several hours, and the precipitate of lead carbonate, washed free from sodium, was dissolved in nitric acid and united to the

<sup>1</sup> A fuller description of the details is to be found in the paper by S. Radcliff, *Jour. and Proc. of the Roy. Soc. of New South Wales*, 47, 145 (1913).

<sup>2</sup> *THIS JOURNAL*, 38, 223 (1916).

main portion of the nitrate, which was recrystallized four times from pure water and precipitated as chloride from a warm solution in a quartz dish with hydrogen chloride. The precipitate was centrifuged, dissolved in water in a large platinum can and recrystallized four times, each time having added a few drops of hydrochloric acid to prevent the formation of basic salt. The second mother liquor gave no test for nitrate. This chloride, dried over caustic alkali, formed Sample A, and after two additional recrystallizations a smaller specimen constituted Sample B.

The second portion of the original nitrate made from the Australian sample was purified in a much simpler fashion. Avoiding the troublesome precipitation with hydrogen sulfide, we recrystallized the nitrate five times successively by adding concentrated nitric acid to its aqueous solution; then the radio-lead was converted into chloride, and by precipitation with excess of hydrochloric acid this salt also was recrystallized five times. This was Sample C of the chloride, a portion of which before the last crystallization had served to prepare Sample D of the metallic radio-lead used for determining the density.<sup>1</sup>

The next sample, designated F, was prepared from American carnotite by the Standard Chemical Co., of Pittsburgh, and came to us through the kindness of Dr. C. H. Viol, of this company, and of Professor W. D. Harkins, of the University of Chicago. After one or two recrystallizations as nitrate and three consecutive separations as chloride, this material had been reduced to metal by fusion with alkaline tartrate and carbonate, and reached us in this form. Harkins had determined its grating spectrum, and found no lines foreign to ordinary lead. Recrystallization as nitrate and chloride having been so efficacious in the case of Sample C, we continued the same method here, recrystallizing this sample thrice successively in the form of each of these salts. The limitation in the amount of material prevented further purification.

Two other samples of especial value and significance were obtained through the kindness of Dr. Ellen Gleditsch, of Kristiania. Both came from primary rocks—Norwegian pegmatite dykes. The purification of one of these, from cleveite, has already been described;<sup>2</sup> the source of this material, which occurred in cubic crystals and was carefully selected, was near Langesund, Norway. It was recrystallized first as nitrate and then as chloride three times each, in the usual manner; and the pure substance, dried in a vacuum over caustic alkali, was designated as Sample G.

Yet another sample, designated H, was prepared from lead sulfide, also kindly sent by Dr. Gleditsch, obtained from selected crystals of Norwegian octahedral bröggerite from Roade, near Moss, Norway. This was purified in precisely the same way as lead from cleveite.

<sup>1</sup> *Loc. cit.*, p. 224.

<sup>2</sup> Richards and Wadsworth, *THIS JOURNAL*, 38, 1659 (1916).

In addition to these four samples of radio-lead enough ordinary lead was carefully purified to serve as the basis of control-analyses. The purest "test lead" of commerce, free from silver, was dissolved in nitric acid, and recrystallized four times as nitrate and four times as chloride.

Throughout this work the usual care taken in atomic weight investigations was not forgotten. The nitric acid, hydrochloric acid, water and silver were all purified in methods already often described, and throughout the work on the nitrate and chloride of lead (except in the preparation of the nitrate for Sample A), the material was treated exclusively in vessels of platinum or quartz. In the case of Sample A, vessels of a good modern, slightly soluble glass, were employed.

None of our preparations after ignition in hydrochloric acid was entirely free from a trace of the insoluble black residue usually left by even carefully purified fused lead chloride when it is dissolved in water. This difficulty has been already met with by Baxter and his assistants, as well as in the earlier work on radio-lead.<sup>1</sup> In many cases the amount of contamination was almost if not wholly negligible; in others, on the other hand, it was appreciable. The amounts found in the two analyses of ordinary lead detailed below were, respectively, 0.26 and 0.30 mg., whereas the amounts found in the nine analyses of radio-lead were, respectively, 0.84, 0.21, 1.95, 0.00, 0.05, 0.47, 0.04, and 0.00 mg. These quantities, found by collecting the black residue on a Gooch-Munroe crucible before precipitation of chlorine with silver, were subtracted from the initial weight of the fused lead chloride. It is noticeable that in general those preparations which contained appreciable amounts of the residue were slightly lower than the others as regards the final atomic weight obtained, but this conclusion rests on only a few cases and may have no significance. In any case the error produced by this slight residue (which consisted mainly of carbon, with a trace of silica) could not have been important. The residues were of a much smaller order than the differences between the atomic weights of the various samples, and the main outcome of the work would have been unaffected if they had been entirely disregarded.

The black residue may be entirely eliminated by adopting a method which has been in use for a long time for freeing fusible salts from silica, namely, the preliminary fusion of the salt, filtering off the residue, and recrystallizing before the analysis is commenced.<sup>2</sup> Hönigschmid and St. Horovitz<sup>3</sup> have shown also that by distillation in quartz this residue remains behind, a fact which we have recently verified.

<sup>1</sup> Richards and Lambert, *THIS JOURNAL*, 36, 1336 (1914).

<sup>2</sup> See Stas, "Untersuchungen Über die Gesetze der Chemischen Proportionen. Über die Atomgewichte und Ihre Gegenseitigen Verhältnisse," Leipzig, 1867, p. 275; Richards, *THIS JOURNAL*, 24, 376 (1902); see also Baxter and Hartmann, *Ibid.*, 37, 117 (1915).

<sup>3</sup> Hönigschmid and St. Horovitz, *Sitzb. k. Akad. Wiss. Wien, IIa*, 123, 16 (1914).



The method of analysis was essentially similar to that so often described. The lead chloride was fused in a platinum boat in pure hydrogen chloride; this gas was displaced by nitrogen while the substance was cooling; and finally the pure dry salt in its boat was pushed into the weighing bottle, stoppered in pure dry air with the help of the familiar "bottling apparatus," and weighed at leisure. The weighed salt was placed in a large Erlenmeyer flask with glass stopper very carefully ground. Enough water was then added to form a fiftieth-normal solution of the salt and the flask and contents, with the addition of a drop of pure nitric acid to prevent the formation of basic salt,<sup>1</sup> were gently warmed on an electric stove, at about 50°, until complete solution was obtained. The boat was then removed, and the residue filtered off, both boat and residue being carefully washed and the filtrate being collected directly in the precipitating flask.

The chlorine contained in this solution was then precipitated in the usual fashion by an amount of silver calculated as nearly as possible to correspond with it. Especially in the early determinations of a previously untested sample the exact amount was not attained, and more silver or more chloride had to be added, but in most of the subsequent cases the precipitation was found at once to be almost complete. These small quantities of silver, or those corresponding to the additional chloride, were, respectively, added to or subtracted from the weight of silver originally taken in each case, and the finally corrected weight is given in the table. As the magnitudes of these small quantities are purely accidental, their detailed recital is unnecessary. The precipitation was carried on in a dark room, under red light, and the usual precautions were taken. The attainment of exact equivalence of silver and chlorine was tested in a nephelometer in the customary fashion.

The balance used was a good one, and the weights were, of course, carefully standardized. All the weighings were reduced to the vacuum standard (adding 0.060 mg. for each gram of lead chloride and subtracting 0.030 mg. for each gram of silver) and all other precautions usual in this sort of work were carefully maintained.

The first two determinations on ordinary lead were only preliminary, in order to gain practice with the method, and are not included in the table below. They yielded as values for the atomic weight, respectively, 207.15 and 207.16. All the other analyses which were brought forward to conclusion are recorded in the tables. Probably the first analysis in the second table of Sample A of Australian carnotite was somewhat erroneous, but the effect on the average, in which it was included, is unimportant. The tables are self-explanatory. The atomic weights of silver and chlorine are taken as 107.88 and 35.459, respectively.

<sup>1</sup> See Baxter and Grover, *THIS JOURNAL*, 37, 1027 (1915).

## THE ATOMIC WEIGHT OF ORDINARY LEAD.

Sample.	Corrected weight PbCl <sub>2</sub> .	Corrected wt. Ag added.	Ratio PbCl <sub>2</sub> : Ag.	Atomic weight Pb.
3.....	3.72918	2.89325	1.28892	207.179
4.....	5.35111	4.15151	1.28896	207.188

Average, 207.183

## THE ATOMIC WEIGHT OF RADIO-LEAD.

Sample.		Corrected weight PbCl <sub>2</sub> .	Corrected wt. Ag added.	Ratio PbCl <sub>2</sub> : Ag.	Atomic weight Pb.
1 A	Carnotite, Australia.....	4.64010	3.61118	1.28493	206.318
2 B	Carnotite, Australia.....	5.35517	4.16711	1.28512	206.359
3 B	Carnotite, Australia.....	6.15608	4.79072	1.28500	206.334
4 C	Carnotite, Australia.....	4.14770	3.22748	1.28512	206.359

Average, 206.342

5 F	Carnotite, U. S. A.....	5.31585	4.12670	1.28816	207.015
6 F	Carnotite, U. S. A.....	4.65899	3.61707	1.28806	206.994

Average, 207.004

7 H	Bröggerite, Norway.....	4.29104	3.34187	1.28402	206.122
8 G	Cleveite, Norway.....	3.92736	3.05913	1.28382	206.079
9 G	Cleveite, Norway.....	4.45270	3.46818	1.28387	206.090

Average, 206.084

The results of these analyses show that the different samples of radio-lead all give lower values for the atomic weights than ordinary lead, but that the material from each source gives a different value, precisely as had been previously found in the earlier investigations in this and other laboratories. Summarized, the results were as follows:

## ATOMIC WEIGHT OF RADIO-LEAD.

Ore.	Geographical origin.	Atomic wt.
Galena (?)	American ordinary lead	207.18
Carnotite	Colorado, U. S. A. (?)	207.00
Carnotite	Radium Hill, N. S. W., Australia	206.34
Bröggerite	Moss, Norway	206.12
Cleveite	Langesund, Norway	206.08

In this table results have been arranged in order of the atomic weight. Ordinary lead gave the maximum value (essentially equal to that found by Baxter and Grover<sup>1</sup>; and Norwegian cleveite gave the minimum value (essentially equal to that found by Hönigschmid in bröggerite,<sup>2</sup> 206.06).

It seems reasonable to suppose that the other samples were composed of mixtures of these two kinds of lead, but that is by no means certain, for there may be yet a third variety. The Norwegian bröggerite gave a result so near to that of the cleveite that we may assume the substance to be almost of the same kind, with but very slight admixture of an im-

<sup>1</sup> Baxter and Grover, *THIS JOURNAL*, 37, 1027 (1915).<sup>2</sup> Hönigschmid and St. Horovitz, *Sitzb. k. Akad. Wiss, Wien, IIa*, 123, 1 (Dec., 1914).

purity; but the two carnotites give widely divergent results. The lead from Australian carnotite was known to have originated partly from an admixture of galena; therefore it was to be expected that the atomic weight would be greater than the minimum value for radio-lead. Its value, 206.34, would be given approximately by a mixture of three parts of radio-lead like that obtained from Norwegian cleveite with one part of ordinary lead—a reasonable supposition, since, as stated above, the Australian carnotite was known to have contained galena. The American carnotite, Sample F, represented by Analyses 5 and 6, is more puzzling. This has an atomic weight which would be given by a mixture of only one part of radio-lead with 5 or 6 of ordinary lead, a condition which seems to indicate the admixture of very large amounts of galena with the sample in question. Since the source is uncertain one cannot say whether or not this inference is satisfactory. The alternative would be the assumption of an admixture of a third kind of lead with yet higher atomic weight, such as that possibly indicated by the work of Soddy and Hyman.<sup>1</sup>

Two physical properties of the several preparations under consideration have especial interest, namely, the magnitude of the radioactivity and the nature of the spectrum.

One of us, in collaboration with Dr. Lemberg, had already concluded that the radioactivity is not proportional to the decrease in atomic weight in samples of radio-lead coming from different sources, and our present experience fully confirms this conclusion. The radioactivity of the several samples was determined by the rate of fall of a gold-leaf spectroscope arranged in the usual fashion so as to measure quantitatively the rate of fall of the gold leaf by means of a small telescope. Equal weights of the several samples of lead chloride spread out in a thin layer were tested in succession. The rate of the fall of the instrument in the absence of any radioactive substance was subtracted from that in the presence of each. Alpha radioactivity was excluded by thin aluminum foil; that which was measured was due almost entirely to beta-rays. The results are given by the following table:

TABLE.

Source of radio-lead.	Time of fall in seconds.	Rate of fall.		
		Per minute.	Natural.	Corrected.
Australian Carnotite.....	9.45	0.1053	0.0287	0.0766
Norwegian Bröggerite.....	4.02	0.2487	0.0287	0.2200
Norwegian Cleveite.....	....	....	....	0.1638 <sup>2</sup>
American Carnotite.....	1.79	0.5587	0.0287	0.5300
Uranium Oxide.....	11.73	0.0850	0.0287	0.0563

If the radioactivity were dependent upon the presence of radium G (the supposed end product of the decomposition, a form of metallic lead),

<sup>1</sup> *Loc. cit.*

<sup>2</sup> Calculated from data from another electroscope.

the rate of fall for cleveite would be the greatest and that for American carnotite the least. But the results are precisely the other way about. There can be little question, then, that radioactivity is not due to the isotope which gives the low atomic weight. Probably it is due to radium E, since in all of our samples the half-value of the radioactivity was attained in about five days—the half life of radium E. The maximum value, approached asymptotically, is nearly reached in a month.

The spectrum of radio-lead as thus far studied by Hönigschmid, by Merton and by Harkins, as well as by Baxter (who kindly photographed the ultraviolet spectrum of one of the samples of lead prepared by one of us with the help of Dr. Lember) has always been found to be essentially like that of ordinary lead. In the present research we thought it worth while once more to test this question and especially to extend the inquiry to the visible portion of the spectrum—most of the tests in the past having been made in the ultraviolet region. We found difficulty in eliminating traces of copper, silver and calcium too small to be detected by ordinary analysis, either quantitative or qualitative. The extreme delicacy of the spectrum in a Féry spectrometer was shown by the fact that Sample C of Australian lead, which gave distinct silver lines, nevertheless showed no trace of this metal when dissolved in nitric acid and tested nephelometrically with bromide for the presence of silver, although the latter test is a very sensitive one. The amount of silver giving these strong lines must, therefore, have been at least as small as is represented by the very slight solubility of silver bromide in the presence of excess of bromine ion—far too little to affect the atomic weight. After eight recrystallizations as nitrate and two as chloride, the product gave in every respect precisely the same spectrum as the purest ordinary lead prepared by Baxter and Grover, except for a vanishingly small trace of two of the most prominent silver lines.

The details of the spectroscopic testing were as follows: To make the electrodes, electrolytic crystals were dried on pure filter paper and fused in a current of pure hydrogen in a hard glass (or silica) tube constricted at one end to the desired size. The molten metal was allowed to run into the constricted part of the tube. If the glass adheres to the metal the surface of the lead must be carefully freed from fragments when the glass is removed, preparatory to use in the spectroscope.

Between two electrodes thus prepared, 2 mm. apart, were flashed sparks from a large induction coil. As usual, a large condenser, placed in parallel with the coil, increased the strength of the spark; and a small self-inductance (consisting of a number of turns of coarse insulated wire) served to eliminate air lines. The spark must be intermittent, otherwise the leaden electrodes will melt; its light was focused on the slit of the spec-

troscope by means of a double convex spherical-cylindrical lens, of quartz or glass, as the need required.

The photographs of the ultraviolet region in the Féry spectrometer were very kindly made by Professor Baxter. Photographs of the visible portion of the spectrum were made by us in the Gibbs Laboratory (by means of a less technically complete, but nevertheless fully satisfactory, spectrometer). The range of this latter spectroscopy was between wave lengths 3300 and 7800—the permeability of glass limiting the effect on one end and the sensitiveness of the specially prepared plate on the other. All the latter work of loading and developing had to be done in complete darkness. To make assurance doubly sure, a further study of the visible spectrum was made, in collaboration with Mr. Norris F. Hall, with the help of the Hilger wave-length spectrometer, comparing visually in the same field of view the spectra of pure ordinary lead and the best purified specimen from Australian carnotite. Every line was scrutinized between the range 4000 and 7600, especial pains being taken in the red and yellow portions, the least satisfactory from a photographic point of view. No discernible differences between the two spectra were observed.

The lead kindly sent us by Professor Harkins was also found to be identical in every respect to the other two samples, except for a faint trace of copper. The lead made from the Norwegian cleveite had been less often crystallized; it showed a distinct trace of silver, and minute traces of copper and calcium; but (so far as we could tell) no impurity in amount sufficient to affect the atomic weight.

Because no lines were detected between wave lengths 7800 and 2200 in any of the samples which were not due either to ordinary lead or to unimportant traces of well-known impurities, the conclusion previously reached by Richards and Lambert is supported, namely, that radio-lead possesses the same spectrum as ordinary lead. The present confirmation is especially interesting because of the support of the presumably almost pure radio-lead obtained from the preparations of Dr. Gleditsch.

Since the atomic weight is variable, but the spectrum of these samples all the same, one must conclude that a part of the atom exercising an important effect upon the atomic weight is without influence upon the spectrum or the volume. The dual nature thus postulated is, of course, in accord with the interesting hypothetical assumptions which have been advanced on various sides concerning the possible make-up of the atom; but our present research can go no further than support the idea of duality without defining exactly of what the two parts may consist. Nothing in the outcome is in any way inconsistent with the suggestive disintegration hypothesis, independently advanced by Soddy and Russell in England and by Fajans in Germany.

We are glad to acknowledge our indebtedness to the Carnegie Institution of Washington for generous support in this investigation.

### Summary.

In this paper the atomic weight of four different samples of radio-lead not hitherto tested, as well as one sample of ordinary lead (used to control the others) was determined. The results were as follows:

Ordinary lead.....	207.18
Radio-lead (Colorado).....	207.00
Radio-lead (Australia).....	206.34
Radio-lead (obtained from bröggerite from Norway).....	206.12
Radio-lead (obtained from cleveite from Langesund, Norway).....	206.08

That the most carefully selected sample should give the lowest result is strong evidence that the higher results obtained from other samples were due merely to the accidental admixture of ordinary lead. As before, no new lines were found either in the ultraviolet or visible spectrum of any of these samples. Hence the atom of lead may be supposed to have a dual structure. Each sample, except the ordinary lead, possessed radioactivity, but the magnitude of this radioactivity seemed to bear no relation to the lowering of the atomic weight.

CAMBRIDGE, MASS., 1914-1916.

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[CONTRIBUTION FROM THE LABORATORY OF QUALITATIVE ANALYSIS, COLLEGE OF THE CITY OF NEW YORK.]

## THE SYSTEMATIC DETECTION OF THIOCYANATES.

BY LOUIS J. CURTMAN AND BEN R. HARRIS.

Received September 23, 1916.

**Nature of the Problem.**—One of the most striking reactions in qualitative work, is the red color produced when ferric salts and thiocyanates are brought together in solution. While the production of this red color serves as an exceedingly sensitive test for iron, as a test for thiocyanates this reaction is not only of a much lower order of sensitiveness,<sup>1</sup> but is also interfered with by many acids. Arsenates, phosphates, oxalates, tartrates, fluorides<sup>2</sup> and borates<sup>3</sup> hinder the free course of the reaction; ferrocyanides mask the red color, while iodides, acetates and nitrites offer the most serious interferences by forming colorations with ferric salts similar to the color of ferric thiocyanate.

<sup>1</sup> This was to be expected; for, Kruss and Moraht (*Ber.*, 22, 2056 (1899)) have demonstrated that the maximum color is produced when ferric chloride and potassium thiocyanate are brought together in the proportion of 1 : 12, respectively, a condition that is not reproducible when unknown and minute amounts of thiocyanate have to be dealt with. Quantities of thiocyanates in excess of this ratio also produce the maximum color, so that in testing for iron it is always possible to produce the deepest color attainable in a given case.

<sup>2</sup> Stokes and Cain, *Bull. Bur. of Standards*, 3, No. 1, 115 (1907).

<sup>3</sup> Prescott and Johnson, *Qual. Chem. Anal.*, 1918, p. 155.

**Determination of the Sensitiveness of the Test.**—To determine the sensitiveness of the test for thiocyanates, which depends upon the formation of ferric thiocyanate, a definite volume of a standard solution of potassium thiocyanate was treated in a test tube, with 0.5 cc. 2 *N* ferric chloride solution,<sup>1</sup> the whole diluted to 5 cc., shaken, allowed to stand one minute and observed. The results obtained are given in Table I.

TABLE I.

No.	Mg. SCN.	Result.
1-2	5-3	Deep blood red
3-4	1-0.5	Deep red
5-6	0.4-0.3	Brownish red
7	0.2	Light brownish red
8	0.1	Reddish yellow (limit)

An inspection of Table I will show that 0.1 mg. of thiocyanate may be detected with the ordinary amount of care.<sup>2</sup> The addition of three drops of concentrated hydrochloric acid had practically no effect on the color.

For a reason stated below,<sup>3</sup> numbers 1, 3 and 8 of Table I were repeated, using ferric nitrate and 3 drops of 10% nitric acid in place of ferric chloride and hydrochloric acid, respectively. Results identical with those recorded in Table I were obtained.

It may be of interest to state that while in the detection of minute amounts of iron, the test may be considerably intensified by extracting the ferric thiocyanate with ether, this procedure is of no value when conditions are reversed. In Experiments 3-8, Table I, colorless ether layers were obtained when the solutions were shaken first with 2 and then with 5 cc. of ether, the aqueous layers retaining their original colors. This is probably due to the fact that in the test for iron there is invariably added a large excess of thiocyanate, while in the experiments noted above this was not the case.

**Extent of Interferences.**—To determine the extent to which iodides, acetates and nitrites interfere with the test for thiocyanates, a series of experiments was conducted. The procedure was the same as that followed in the determination of the sensitiveness of the test. The results obtained are recorded below in Tables II, III and IV.

TABLE II.  
Interference of Iodides.

No.	Mg. I.	Result.
1	30	Blood red
2-3	20-15	Dark brownish red
4-5	10	Light brownish red
6	8.5	Light brownish red
7-8	7	Yellowish red (limit)
9	0.0	Very faint yellow

TABLE III.  
Interference of Acetates.

No.	Mg. C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> .	Result.
1-2	100-50	Deep blood red
3-4	30-25	Reddish brown
5-6	20	Light reddish brown
7-8	18	Reddish yellow (limit)
9-10	0.0	Very pale yellow

<sup>1</sup> This solution contained 0.5 cc. conc. HCl per liter.

<sup>2</sup> This figure is also given by A. A. Noyes, *Qual. Chem. Anal.*, 1915, p. 101.

<sup>3</sup> See number eight under "Comments on the Procedure."

TABLE IV.  
Interference of Nitrites.

No.	Mg. NO <sub>2</sub> .	Result.
1	100	Brownish red ppt.
2-3	50-35	Dark reddish brown
4-6	25-17	Brown
7-8	14	Light brown (limit)
9-10	11	Brownish yellow

**Comments.**—It is evident that iodides rank first in the degree of interference. It may be of interest to note that the colorations produced both by large and small amounts of iodide are almost identical in tint with those produced by certain corresponding quantities of thiocyanate, whereas the colorations produced by small amounts of acetate and of nitrite resemble the color of ferric thiocyanate less closely. It is for this reason, that it was difficult to determine the "limit" interferences of these acids. The limit data, especially in Table IV, are therefore only approximate. In the tables, the limit of interference is that quantity of the substance which produces a coloration equivalent to that formed under similar conditions by 0.1 mg. of thiocyanate. The ferric chloride solution mentioned contained 0.5 cc. of concentrated hydrochloric acid per liter to retard hydrolysis. This free acid decomposed the nitrite, hence, a special, nearly neutral 2 *N* ferric chloride solution was used in the determination of the interference of nitrites. Even this solution caused a slight evolution of the oxides of nitrogen. The coloration given by iodides was unaffected by the addition of three drops of concentrated hydrochloric acid. The same quantity of acid, however, bleached to a greenish yellow, the coloration given by acetates.

**The Available Methods for the Detection of Thiocyanates in the Presence of Iodides.**—A search of the literature failed to disclose a direct method for the separation of iodides from thiocyanates.<sup>1</sup> The liberation of iodine and its removal by means of carbon disulfide or some similar solvent is the only means for this purpose. Of the many liberators of iodine, *e. g.*,  $\text{KMnO}_4$ ,  $\text{H}_2\text{O}_2$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{KNO}_3$ ,  $\text{Cl}$ -water and  $\text{FeCl}_3$ , only the last named was suitable; for, while they all adequately liberated the iodine,

<sup>1</sup> After the completion of this work, our attention was called to a paper by Benedict and Snell (THIS JOURNAL, 27, 738), entitled "A Method for the Detection of the More Common Acids," in which the separation of thiocyanates from iodides is effected by digesting the precipitate of  $\text{AgI}$  and  $\text{AgSCN}$  "in the cold with a mixture of three volumes of 2 *N* sodium chloride and one volume of 5 *N*  $\text{HCl}$ ." To determine whether this method possessed any advantage over the one proposed by us, test experiments were made, a description of which appears in Note 4, page 2625. While this paper was in press, Weber and Winkelman (THIS JOURNAL, 38, 2000) published a paper in which the separation of  $\text{I}$  and  $\text{SCN}$  is effected by heating their silver salts with sodium formate in alkaline solution. By this process the  $\text{AgSCN}$  is reduced giving metallic silver and sodium thiocyanate while  $\text{AgI}$  is not reduced.



they also oxidized the thiocyanate to cyanide and sulfate, thus vitiating the subsequent ferric thiocyanate test. Even the use of ferric chloride did not yield satisfactory results, owing to the fact that the extraction with carbon disulfide was cumbersome and that the removal of the excess of iron which it was necessary to introduce at the beginning, entailed serious difficulties.

Advantage was also taken of the fact that nascent hydrogen reacts with thiocyanates to give hydrogen sulfide.<sup>1</sup> The evolution of hydrogen sulfide would thus serve as a suitable, though indirect, means for the detection of thiocyanates in the presence of iodides, acetates and nitrites, subsequent to the removal of all other sulfur compounds capable of liberating hydrogen sulfide under similar conditions. This method was tried but was abandoned on account of the excessive sensitiveness of the test and because of its inability to indicate the quantity of thiocyanate present.

The procedure finally adopted and described in detail below depends upon the fact<sup>2</sup> that silver iodide is for all practical purposes inert in a hot 5% sodium chloride solution, while silver thiocyanate is transposed to sodium thiocyanate and silver chloride<sup>3</sup> by this treatment.<sup>4</sup> Acetates and nitrites are held in solution by making the preliminary silver precipitation in a boiling, sufficiently dilute solution. The precipitate consisting of silver iodide and thiocyanate<sup>5</sup> is filtered and subjected to the sodium chloride treatment. Other interfering acids are previously removed by precipitating them with a solution of a mixture of barium and calcium nitrates<sup>6</sup> and a solution of cobalt nitrate.<sup>7</sup>

### Procedure.

The solution contained in a 200 cc. beaker is rendered *just* alkaline with sodium hydroxide.  $\text{Ba}(\text{NO}_3)_2 + \text{Ca}(\text{NO}_3)_2$  and  $\text{Co}(\text{NO}_3)_2$  are added in excess in the order named. About 3 g. of washed asbestos fiber are introduced, the mixture boiled for  $\frac{1}{2}$  minute with stirring, filtered on a

<sup>1</sup> Fresenius, "Manual of Qual. Chem. Anal.," Well's translation, p. 372 (1898).

<sup>2</sup> A number of experiments was made to test this point. See also Nos. 1 and 2, Table V.

<sup>3</sup> Some of the  $\text{AgCl}$  so formed is dissolved by the excess of  $\text{NaCl}$ .

<sup>4</sup> As this transposition was similar to that employed by Benedict and Snell (see Note 1, p. 2624) experiments were made to ascertain which of the two was the more efficient. Two separate precipitates each consisting of a mixture of 500 mg. of  $\text{I}$  as  $\text{AgI}$  and 1 mg. of  $\text{SCN}$  as  $\text{AgSCN}$  were treated, respectively, by the two procedures. The conditions were kept uniform as to volume and the quantity of  $\text{FeCl}_3$  added. With the Benedict and Snell method a solution having an orange-yellow color was finally obtained; whereas our procedure gave as the final result a dark brownish red solution affording unmistakable evidence of the presence of  $\text{SCN}$ .

<sup>5</sup> Silver chloride and bromide are also filtered off at this point.

<sup>6</sup> 50 g.  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  were dissolved in 100 cc. water. This solution was then saturated with  $\text{Ba}(\text{NO}_3)_2$ .

<sup>7</sup> This solution contained 25 g.  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in 100 cc.

fluted filter and washed with hot water till the washings are only faintly pink. The filtrate and washings, received in a 150 cc. beaker, should have a volume of about 100 cc. The filtrate is rendered acid with 5 drops 10%  $\text{HNO}_3$  and  $\text{AgNO}_3$  solution<sup>1</sup> added in excess. The reaction mixture is boiled for one minute with stirring to prevent loss by bumping, filtered<sup>2</sup> and washed with hot water till the washings are no longer pink. The precipitate, together with part of the filter paper to which the precipitate adheres, is returned to the beaker in which the silver precipitation was made, 10 cc. of 5%  $\text{NaCl}$  solution are added, the mixture kept near the boiling point for 3 to 5 minutes with vigorous stirring, filtered on a very small filter and washed twice with hot water, catching filtrate and washings in a 50 cc. evaporating dish. The combined filtrate and washings are concentrated by evaporation to about 4 cc., transferred to a test tube, acidified with 1 drop 10%  $\text{HNO}_3$  and finally treated with 0.5 cc. 2 *N* ferric nitrate.

**Comments on the Procedure.**—1. The  $\text{Co}(\text{NO}_3)_2$  precipitates sulfides, cyanides, ferrocyanides and ferricyanides, thereby materially reducing the size of the silver precipitate and supplying a separation of thiocyanates from ferrocyanides. The nitrates of Co, Ba and Ca were employed in preference to the chlorides to render the silver precipitate as small as possible.

2. The asbestos fiber is added to facilitate the filtration of cobalt cyanide, ferrocyanide and ferricyanide. The asbestos also serves to indicate the presence of an excess of  $\text{Co}(\text{NO}_3)_2$  which is not otherwise visible. If allowed to drop gently and float on the surface of the liquid, the asbestos will acquire a pink color when cobalt is present in excess. Furthermore the asbestos prevents bumping when the mixture is boiled.

3. The silver precipitate may well be washed by decantation, the bulk of the precipitate being retained in the beaker for the  $\text{NaCl}$  treatment.

4. In test analyses 12–24 where the silver precipitate consisted almost exclusively of 1 mg. of thiocyanate as  $\text{AgSCN}$  in a volume of 110 cc., there was visible only a faint opalescence which required a second filtration. Care should be taken always to obtain a perfectly clear filtrate from the silver precipitate, refiltering if necessary. It is safer in any case to refilter because the pink color resulting from the presence of Co, may mask the opalescence.

5. It is imperative that the silver precipitate be washed free of cobalt because the pink color of the latter may be mistaken for ferric thiocyanate in the final test.

6. A confirmatory test was always made with  $\text{HgCl}_2$  solution. With small amounts of  $\text{SCN}$ , the decolorization with  $\text{HgCl}_2$  is even a better indication of the presence of the acid than the original red or reddish color.

7. Since thiosulfates are only incompletely precipitated by barium, on the addition of silver nitrate, first a yellow and finally a black precipitate of  $\text{Ag}_2\text{S}$  separates out. But as evidenced by test analyses 14, 30 and 32, Table V, this precipitate does not interfere with the general procedure.

8. The final test is made in a volume of 5–6 cc. Before the test can be made, however, the solution as a rule will have cooled sufficiently to cause some of the dissolved  $\text{AgCl}$  to separate out, thus causing the solution to become turbid. The addition

<sup>1</sup> 6.45 g.  $\text{AgNO}_3$  were dissolved in 100 cc. of water, yielding a solution containing 50 mg. Ag per cc.

<sup>2</sup> A 9 cm. S. & S. No. 590 filter is required for this purpose.

of  $\text{FeCl}_3$  augments this turbidity; hence the use of  $\text{Fe}(\text{NO}_3)_3$ . The cloudiness, however, may be diminished and in most cases entirely removed by warming, the rise in temperature causing the  $\text{AgCl}$  to redissolve.

**Test Analyses.**—To test the efficiency of the method a large number of test analyses was made. The results are given in Table V.

**Comments on Table V.**—Following the procedure, thiocyanate was found in test analysis No. 26, although none was introduced. This result, however, does not militate against the method for the reason that thiocyanate, although not originally added, was nevertheless formed in solution from the interaction of sulfides and cyanides or of the polysulfide in the sulfide solution, and cyanides. It was therefore considered necessary to avoid the simultaneous presence of sulfides and cyanides in further experiments. The same may be said of thiosulfates as evidenced by the result obtained in test analysis 28. Prescott and Johnson<sup>1</sup> state that thiocyanate is formed in the fusion of cyanides with thiosulfates; and what holds true for a fusion may be supposed to take place also when the salts are boiled together in solution, though probably in a much lesser degree. The negative results obtained in test analyses 30 and 31, in which the above precautions were observed, showed the method to be thoroughly trustworthy.

**Approximation of the Quantity of Thiocyanate.**—In the course of the work it was observed that with amounts of thiocyanate greater than 4 or 5 mg., the depth of color was such as to make it impossible to approximately estimate with the naked eye the amount of thiocyanate present. Between the colors produced by 5 and 250 mg., there was only a very slight difference in opacity. Between 25 and 250 mg. of thiocyanate there was no discernable difference in the coloration. It was therefore deemed desirable to devise means whereby the quantity of ferric thiocyanate might be roughly estimated. The volume of mercuric chloride solution<sup>2</sup> required to discharge the red color affords such means. Attempts to bleach the color completely by comparison with a blank were unsuccessful because of the disproportionately large amount of mercuric chloride required to remove the last tinge of red. Mercuric chloride solution was therefore added only to the point when a certain brown tint was reached; beyond this stage, the bleaching was exceedingly slight with each addition of 0.3 cc. of mercuric chloride, whereas up to this point considerable changes in color were produced by the same small quantities of mercury solution. With very large amounts of thiocyanate the changes on first adding the mercuric chloride are not visible; but this state of no apparent change is easily distinguished from that alluded to above, by

<sup>1</sup> "Qualitative Chemical Analysis," p. 272 (1908).

<sup>2</sup> It was found necessary to use a highly concentrated solution because dilution alone discharges the red color. To dissolve 27 g.  $\text{HgCl}_2$  in 100 cc. of water, it was necessary to add 10 g.  $\text{NaCl}$ . The resulting solution contained 200 mg.  $\text{Hg}$  per cc.

TABLE V.—TEST ANALYSES.

No.	SCN.	I.	C <sub>6</sub> H <sub>5</sub> O <sub>4</sub> .	NO <sub>3</sub> .	Cl.	Br.	F.	CN.	Fe(CN) <sub>2</sub> <sup>III</sup> .	Fe(CN) <sub>2</sub> <sup>IV</sup> .	S <sub>2</sub> .	SO <sub>3</sub> .	C <sub>6</sub> H <sub>5</sub> O <sub>4</sub> .	PO <sub>4</sub> .	SO <sub>3</sub> .	CO <sub>2</sub> .	SiO <sub>2</sub> <sup>1</sup> .	AsO <sub>4</sub> .	BO <sub>3</sub> .	ClO <sub>3</sub> .	CO <sub>3</sub> .	Result.	Effect of HgCl <sub>2</sub> .
1-1a	0.0	500	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	Negative	No change
2	1.0	500	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	Blood red	Bleached to yellow
3-3a	0.0	500	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	Negative	No change
4	1.0	500	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	Blood red	Bleached to yellow
5	0.0	...	500	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	Negative	No change
6	1.0	...	500	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	Blood red	Bleached to yellow
7	0.0	200	...	...	...	...	...	...	50	50	200	...	...	...	...	...	...	...	...	...	...	Negative	No change
8	0.0	200	100	...	...	...	...	50	100	50	...	...	...	...	...	...	...	...	...	...	...	Distinct brownish red	Bleached to yellow
9	1.0	300	50	...	...	...	...	50	50	50	...	...	...	...	...	...	...	...	...	...	...	Distinct brownish red	Bleached to yellow
10	1.0	250	50	...	...	...	...	...	50	50	100	...	...	...	...	...	...	...	...	...	...	Distinct brownish red	Bleached to yellow
11	1.0	100	50	...	100	150	...	...	50	50	...	...	...	...	...	...	...	...	...	...	...	Blood red	Bleached to yellow
12	1.0	...	...	...	...	500	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	Blood red	Bleached to yellow
13	1.0	...	...	...	...	...	...	1.0	...	...	500	...	...	...	...	...	...	...	...	...	...	Blood red	Bleached to yellow
14	1.0	...	...	...	...	...	...	1.0	...	...	500	...	...	...	...	...	...	...	...	...	...	Blood red	Bleached to yellow
15	1.0	...	...	...	...	...	...	...	...	...	...	...	500	...	...	...	...	...	...	...	...	Blood red	Bleached to yellow
16	1.0	...	...	...	...	...	...	...	...	...	...	...	...	500	...	...	...	...	...	...	...	Blood red	Bleached to yellow
17	1.0	...	...	...	...	...	...	...	...	...	...	...	...	...	500	...	...	...	...	...	...	Blood red	Bleached to yellow
18	1.0	...	...	...	...	...	...	...	...	...	...	...	...	...	...	500	...	...	...	...	...	Blood red	Bleached to yellow
19	1.0	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	500	...	...	...	...	Blood red	Bleached to yellow
20	1.0	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	500	...	...	...	Blood red	Bleached to yellow
21	1.0	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	500	...	...	Blood red	Bleached to yellow
22	1.0	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	500	...	Blood red	Bleached to yellow
23	1.0	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	500	Blood red	Bleached to yellow
24	1.0	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	Blood red	Bleached to yellow
25	1.0	200	100	20	...	20	...	...	...	50	50	50	...	...	...	...	...	...	...	...	...	Distinct red	Bleached to yellow
26	0.0	100	...	...	...	...	...	50	100	50	200	...	...	...	...	...	...	...	...	...	...	Blood red	Bleached to yellow
27	0.0	25	25	25	25	25	25	25	25	25	...	25	25	25	25	25	25	25	25	25	25	Brown	Appreciably bleached
28	0.0	...	...	...	...	...	...	200	...	...	...	...	300	...	...	...	...	...	...	...	...	Deep blood red	Bleached to yellow
29	0.0	...	...	...	...	...	...	200	...	...	...	300	...	...	...	...	...	...	...	...	...	Negative	No change
30	0.0	25	25	25	25	25	...	...	25	25	25	25	25	25	25	25	25	25	25	25	25	Negative	No change
31	0.0	25	25	25	25	25	25	...	...	25	25	25	25	25	25	25	25	25	25	25	25	Negative	No change
32	1.0	25	25	25	25	25	25	...	...	25	25	25	25	25	25	25	25	25	25	25	25	Distinct red	Bleached to yellow
33	1.0	25	25	25	25	25	25	...	...	25	25	25	25	25	25	25	25	25	25	25	25	Distinct red	Bleached to yellow

<sup>1</sup> The solution used was prepared by saturating with H<sub>2</sub>S a definite volume of a standard solution of NaOH and then adding to the saturated solution an equal volume of the same NaOH solution.

<sup>2</sup> The silicate solution used was prepared by fusing a known quantity of C. P. silicic acid with sodium carbonate.

the presence of a blood red color in the latter as against a brown color in the former. The results recorded in Table VI show that the volume of mercuric chloride solution required to bleach the red color to the point when no further considerable change takes place on adding 0.3 cc., is roughly proportional to the quantity of thiocyanate present. This reaction therefore furnishes a basis for an approximate estimation of thiocyanates.

TABLE VI.

No.	Mg. SCN.	Cc. HgCl <sub>2</sub> solution used.
1.....	5	0.6
2.....	50	5.4
3.....	100	9.9
4.....	250	18.6

**Significance of the Results.**—It has been stated by Kern<sup>1</sup> and confirmed by us that in the presence of thiocyanates, palladium chloride may fail to give a reliable indication of the presence of iodides and that palladium nitrate may fail to give a reliable separation of iodides from chlorides and bromides. The need for a test for thiocyanates in the presence of iodides is therefore evident. Moreover, it is hardly necessary to state that in the presence of alkali halides only, the entire preliminary procedure may be dispensed with in testing for thiocyanates. To the solution, acid with dilute nitric acid, it is only necessary to add silver nitrate, and after filtering to treat the precipitate with sodium chloride solution.

#### Summary.

1. The sensitiveness of the ferric thiocyanate test for thiocyanates has been determined.
2. Data are supplied showing the extent of the interference of iodides, acetates and nitrites.
3. A procedure has been devised for the systematic detection of thiocyanates depending upon the ability of a 5% sodium chloride solution to transpose silver thiocyanate.
4. Numerous tests analyses show the reliability of the method.

### FREE ENERGY AND HEAT CAPACITY.

By JAMES M. BELL.

Received November 20, 1915.

In a recent paper, T. W. Richards<sup>2</sup> writes as follows:

"I was able to show, in cases of certain typical reversible galvanic cells, that when free energy change increases with rising temperature, total energy change decreases, and *vice versa*."

And appended to this is a footnote as follows:

<sup>1</sup> *Chem. News*, 32, 242 (1875).

<sup>2</sup> *THIS JOURNAL*, 36, 2433 (1914).

"That is to say, expressed mathematically  $dA/dT = -n.dU/dT$ , in which A represents free energy, U total energy and  $n$  a number, which was often found to be about 2. Of course  $dU/dT$  is nothing more or less than the change of heat capacity during the reaction. J. M. Bell has questioned the sufficiency of the evidence, but he has neglected to note that although Marignac's data (upon which I relied) were perhaps absolutely not very accurate, they are relatively one to another much more to be depended upon; and in this question relative accuracy alone is concerned. *J. Phys. Chem.*, 9, 402 (1906)."

In the paper<sup>1</sup> referred to by Richards, I showed that the possible errors, whose magnitude Marignac<sup>2</sup> was careful to state, were in some cases so great as to leave an uncertainty in the quantity sought ( $dU/dT$ ) greater than the quantity itself. That there were large errors seems to be admitted by Richards, who, however, now makes the claim that Marignac's data were relatively to one another much more to be depended upon. In reply to this, there are here offered two statements of fact which refute the claim.

(1) Marignac makes no such claim about his own data, for in comparing results<sup>3</sup> by taking differences (exactly as Richards does) he frankly admits a possible error of two units in the third decimal place for each solution, or a possible error of four units in the third decimal place for the differences. If the numbers were relatively accurate, the error should cancel out. Where the signs of the errors are unknown, the possible error in the final result must be considered as the accumulation of all the possible errors. Marignac clearly recognized this point.<sup>4</sup>

(2) In determining the heat capacity of a solution of the composition  $\text{CuSO}_4.200\text{H}_2\text{O}$ , Richards takes the mean of two values given by Marignac:<sup>5</sup> 0.9503 between  $18^\circ$  and  $23^\circ$ , and 0.9528 between  $22^\circ$  and  $53^\circ$ . The very fact that the mean was taken indicates that they were considered as duplicates. They differ by more than two units in the third place of decimals; whereas, in my paper I showed that with an error of one unit in the third place of decimals, there was an uncertainty in the quantity to be determined greater than the quantity itself. The wide difference between numbers considered by Richards as duplicates at once refutes his claim of greater relative accuracy, for this relative accuracy could not be greater than the degree of duplication of results.

UNIVERSITY OF NORTH CAROLINA,  
CHAPEL HILL, N. C.

<sup>1</sup> This reference should be *J. Physic. Chem.*, 9, 381 (1905).

<sup>2</sup> *Ann. chim. phys.*, [5] 8, 415 (1876).

<sup>3</sup> *Loc. cit.*, p. 421.

<sup>4</sup> On page 415 of his paper (*loc. cit.*) Marignac says of individual results: ". . . . la troisième (décimale) peut être déjà affectée d'une erreur de 1 ou 2, rarement de 3 unités." And on page 421 of the same paper he says of differences: ". . . . la limite des erreurs d'observation celles-ci pouvant bien s'élever, entre les deux expériences à  $\frac{80}{10000}$  ou  $\frac{40}{10000}$ ."

<sup>5</sup> *Loc. cit.* p. 418.

### A Reply to the Foregoing Communication.

Of course I heartily agree with Professor Bell in regard to the general proposition suggested by the foregoing note. There is great need of caution that the limits of accuracy of the data should not be overstepped in any conclusion drawn from them. My footnote, to which he takes exception, is not happily expressed. It was, moreover, too brief to express the exact state of the case. Accordingly, I beg leave to withdraw the wording of the four lines concerning Dr. Bell, with apologies to him, and to substitute for these four lines the following more complete and accurate statement:

"Dr. J. M. Bell has questioned the sufficiency of the evidence. It must be admitted that Marignac's data, upon which I depended, leave something to be desired; but, nevertheless, a careful comparison of the figures seems to show that large errors were comparatively rare.<sup>1</sup> This being the case, it seems to me that although such a single comparison among these data as that adduced by Dr. Bell might be subject to an important chance of mistake, nevertheless, when a number of results (with a range as wide as those employed in my reasoning) combine in pointing toward any given verdict, the chances are much in favor of the correctness of the verdict. Marignac's own use of his data justifies this opinion."

A few quotations from Marignac's remarks, following his tables of results, may make this point clear.

"Mais on peut espérer que les erreurs d'expériences se compensant en grande partie sur un aussi grand nombre de déterminations, les conséquences tirées de leur ensemble seront suffisamment justifiées....."

"Mais à côté de ces observations générales, ces expériences prouvent que l'accroissement de la chaleur spécifique est très rapide pour certaines solutions. Ce fait est surtout remarquable pour le sulfate de cuivre, et il m'est impossible de l'attribuer à une erreur, car j'ai fait trois fois, à trois époques différentes, la série entière des déterminations relatives à ce sel, dans les deux conditions de température et je suis toujours retombé sensiblement sur les mêmes nombres dont j'ai indiqué la moyenne....."

"Il est impossible de méconnaître un certain degré de parallélisme dans les diverses séries de sels. Les bases se rangeraient le plus souvent à peu près dans le même ordre....."

<sup>1</sup> Full discussion of this comparison of Marignac's figures would require too much space for the present note. On tabulating his results at different temperatures for the most dilute solutions containing bivalent metals (which alone came into consideration), it appears that an error of even as much as 1 in the third decimal place was probably not frequent. The mean deviation from the average in all these cases (except that of copper sulfate, which received special discussion) is only 0.0003, and one might well conclude that most of the individual values are probably within 0.05% of the truth. Marignac's cautious temperament apparently led him to claim less than he was entitled to claim.

"La différence entre les chaleurs moléculaires du sulfate et du chlorure de potassium est exactement la même que celle qu'on observe entre le sulfate et le chlorure de sodium. . . . ."

"Il y a identité presque absolue de chaleur moléculaire pour les solutions de sulfate et de chromate de potasse, et de même pour celles d'acide sulfurique et d'acide chromique." . . . . etc.<sup>1</sup>

These quotations show that Marignac, while fully recognizing the possibility of occasional wide deviations, had considerable confidence in his final results, and thought them worthy of employment in parallel comparisons involving a number of data. I used Marignac's values (the best data available) for a kind of comparison not unlike that described in the above quotations, and in a spirit essentially in accord with his. I cannot help thinking that they still deserve this degree of confidence. It should be noted, also, that the special case cited by Dr. Bell is one of the very least significant of all those which I used. If all the cases had been so little decisive as this one, I should agree with Dr. Bell, and should never have drawn the conclusion in question. This is a case of statistical reasoning, which depends not upon a few cases, but rather upon the consensus of all.

Further discussion of the matter may well be postponed until Marignac's figures have been verified or disproved by new experimental determinations, already begun.

THEODORE W. RICHARDS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MISSOURI.]

## THE INFLUENCE OF PRESSURE ON SOLUBILITY.

BY HERBERT F. SILL.

Received September 8, 1916.

### Introduction.

Experimental values for the terms involved in the equation  $T dA/dT = Q$  have been applied with good agreement for the processes of fusion and of vaporization in one-component systems. The same is true for vaporization of mixtures (isothermal distillation).

For the important case of change of state in two-component solid-liquid systems (solution and precipitation) complete experimental data have heretofore been lacking.

When both the influence of pressure and of temperature on the solubility of a substance are known, as well as the volume change involved, the relationship  $dA/dT$  is obtainable as the product  $ds/dT dp/ds$  ( $V_2 - V_1$ ). The significance of these terms may be stated as follows:

Let a large amount of saturated solution at the temperature  $T$  be in contact with the solute at the pressure  $p$ . Then  $dp$  represents the increase in pressure necessary to cause one gram more of the solute to pass into

<sup>1</sup> Oeuvres Complet, II, 630, 632. *Ann. chim. phys.*, [5] 8, 421-425 (1876).



solution isothermally and  $dT$  represents the increase in temperature necessary to produce the same result at constant pressure.

Thus far the only accurate measurement of the influence of pressure upon solubility has been made by E. Cohen, Inouye, and Euwen,<sup>1</sup> in an apparatus designed by them and covering a range of 1500 atmospheres. The substances employed were sodium chloride and mannite and their solubilities in water were determined at the constant temperature  $24.05^{\circ}$  and pressures from one to 1500 atmospheres as follows:

Pressure (atmospheres).	Solubility in parts per hundred.	
	NaCl.	Mannite.
1	26.41	17.12
250	26.60	17.30
500	26.76	17.45
1000	27.02	17.63
1500	27.20	17.69

The values for the solubilities obtained by them, when plotted against the pressure, yield smooth curves, concave toward the pressure axis and indicating by their trend a point of maximum solubility for this temperature, at about 2500 atmospheres pressure.

It appears from the table that for these substances a considerable range of pressure is necessary in order that the solubility change may be sufficient to permit a satisfactory calculation of the value  $dp/ds$ .

These investigators did not attempt a comparison of these pressure solubility data, with any experimental values for the other thermodynamic factors

With view to establishing complete data for a case of solution the following experiments were made involving the design and construction of a new type of "pressure bomb" which is extremely simple in operation and permits the withdrawal of the sample for analysis without reducing or otherwise changing the pressure. This was not possible with the apparatus employed by Cohen, Euwen and Inouye, as it was necessary for them to relieve the pressure and open the bomb in order to take the sample for analysis. This was of no disadvantage for the systems employed by them, since during the few minutes required for the above manipulation the solution remained supersaturated to the full degree of the previous equilibrium conditions.

In the case of certain other systems such as ether-water, upon whose investigation the writer is now engaged, the composition of the layers would not remain unchanged during the time necessary to remove the sample after relieving the pressure.

#### The Pressure Bomb.

This was of the nature of a modified U-tube, the two arms of which were made from "Shelby Steel tubing" of 25 mm. bore and 63 mm. external diameter.

<sup>1</sup> *Z. physik. Chem.*, 75, 291 (1910).

The left hand or "reaction chamber" (Fig. 1) was 30 cm. and the right hand or "mercury chamber" 28 cm. in length. These were filed at the ends to a hexagonal form to permit being held with a wrench when the screw-plugs were tightened.

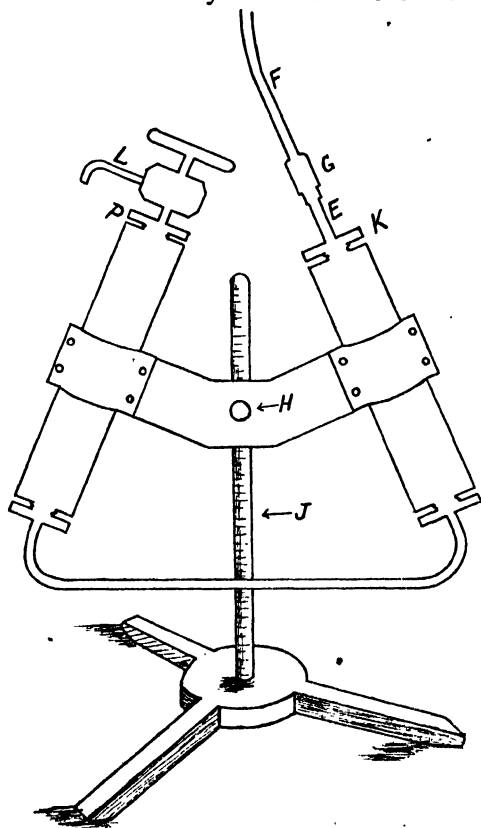


Fig. 1.

The ends of the capillary tubing are threaded and screwed into a steel disc, C, of the same dimensions as the washer and between the two is inserted a rubber washer, B, 3 mm. in thickness and forming a smooth cylindrical surface with the steel disc and washer.

The screw disc is slightly hollowed conically on its outer face to prevent trapping of air when inserted and rests on the shoulder D. When the plug is screwed tight the rubber is forced against the capillary tube and the wall of the bomb chamber.

Connection with the pump is made through the piece of steel capillary E joined to the  $2\frac{1}{2}$  meter flexible copper capillary F by means of the brass coupling G. The bomb is supported in the thermostat by a clamping device so constructed that the whole can rotate freely on the adjustable axis arm H, which can be raised or lowered on the support J. The latter stands within and toward the left end of an oval tank. Through the use

Both chambers were reamed smooth on the inside and turned at each end on the inside for a distance of 40 mm. to a diameter of 31 mm., thus forming a 3 mm. shoulder at D (Fig. 2). These ends were threaded to a depth of 28 mm. for the reception of screw-plugs. The latter were 28 mm. long and provided with enlarged hexagonal heads. The connection between the two chambers and with the Cailletet pump and with the outlet valve is affected by means of capillary steel tubing of 1.5 mm. bore and 6 mm. external diameter. The steel tubing passes first through a 7 mm. hole in the center of the screw-plug, then through a steel washer, A, 6 mm. thick, which fits rather snugly but will slide readily.

of the long flexible copper capillary F, which bends around in a large loop, the bomb can be rotated with little resistance through an angle of more than ninety degrees when connected with the pump, which stands to the right of the tank.

The Cailletet pump, together with its pressure gage, was one of those used in the numerous investigations on compressibility by T. W. Richards and others, and was kindly loaned to the writer for the purpose of the work here presented. The calibration of the gage is fully described in a recent article<sup>1</sup> on the "Compressibilities of Certain Hydrocarbons, Esters, Amines and Organic Halides," and is therein designated as Gage A.

The charging of the bomb is effected as follows:

The upper screw plugs P and K are removed and the apparatus—thoroughly cleaned and dried on the inside—is rotated so that the reaction chamber is in a vertical position and clean mercury is poured in to a depth of about 3 cm., after which the chamber is filled nearly to the top with saturated solution together with a suitable excess of the solid solute. The screw plug P, bearing

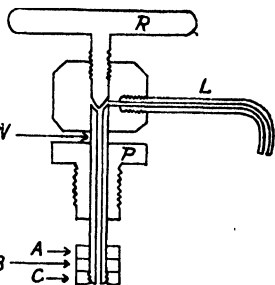


Fig. 2.

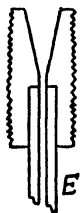
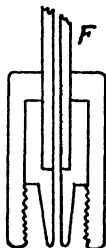


Fig. 3.

the discs, outlet valve, etc., is then inserted with the valve closed and screwed down until mercury appears in the right-hand or mercury chamber. A further amount of mercury is then added, sufficient to half fill the mercury chamber, and the screw-plug P tightly screwed down with a wrench. The outlet valve R is now opened sufficiently to allow a few drops of the solution to escape and insure the expulsion of any air which may have been enclosed, whereupon the valve is tightly closed.

The apparatus is next rotated to the right to allow the mercury chamber to stand vertical and mercury is added to within a centimeter of the shoulder D.

Above the mercury is added a layer of the pump liquid (castor oil was employed in the measurements to be described) to a height about where the screw threads begin. The screw-plug K bearing the short piece of steel capillary E, with its discs and washer, is now inserted in the mercury chamber and screwed down tightly. This forces oil up the capillary and causes it to fill and overflow the conical cavity in the lower

coupling piece.

The upper coupling piece is then held above the lower one and oil from

<sup>1</sup> Richards, Stull, Matthews and Speyers, *THIS JOURNAL*, 34, 972 (1912).

the pump is forced through the long copper capillary and out of the conical tip, whereupon the coupling ring is tightly screwed down. Pressure is now applied from the pump in order to test for leaks and the joints further tightened if necessary.

The apparatus is again rotated to the right so as to place the reaction chamber in a horizontal position. The outlet tube L, made from the steel capillary tubing, is unscrewed, rinsed and dried, replaced and closed at the end by means of a piece of rubber tubing, plugged with a piece of glass rod. This is to prevent the entrance of water from the bath when the apparatus is submerged.

The mercury in the reaction chamber is caused to flow back and forth by means of a simple tilting mechanism. A pulley wheel is placed above the lower end of the horizontal reaction chamber and connected eccentrically with the latter through a brass strip which functions in the manner of a driving rod.

The pulley is so geared that the tilting occurs about every six seconds.

In the following measurements the thermal regulation and the stirring of the bath were connected in the manner described by T. W. Richards.<sup>1</sup>

The regulator was adjusted to  $25^{\circ}$ , measured by means of a Reichsanstalt thermometer graduated in twentieths of degrees, of which the corrections were given to hundredths of degrees. By the use of a reading-lens readings accurate to this fraction could be readily made. A Beckman thermometer graduated in hundredths showed, during all the measurements made, which extended over some seventy hours, a fluctuation of two to three thousandths of a degree.

This excellent constancy is doubtless to be attributed to the use of the hydrogen generator which kept the mercury-platinum contact in an atmosphere of this gas and to the vigorous stirring which was employed.

The first system investigated was sodium chloride and water. This was done with a view to trying out the apparatus and also in order to obtain a comparison with the results obtained by Cohen, Euwen and Inouye.

C. P. sodium chloride was reprecipitated from a saturated water solution by means of HCl gas generated from C. P. acid by the addition from a dropping funnel of C. P. sulfuric acid. The precipitated salt was washed several times by decanting with small amounts of water, dried and heated for an hour at  $350^{\circ}$ . A solution containing about a gram of this product remained colorless on addition of phenolphthalein and turned pink on the addition of one drop of 0.05 *N* sodium hydroxide solution.

The bomb was charged in the manner described and the tilting mechanism set in operation.

In Expt. 1 no pressure was applied from the pump. The tilting was con-

<sup>1</sup> Stähler, "Handbuch der Arbeitsmethoden in der anorganischen Chemie," III,

tinued for two hours and the first sample withdrawn, after which the apparatus was tilted for an additional hour and the second sample taken. The identity in the analytical results on the two samples indicates that saturation was complete in the first case, hence in the following measurements on this system the tilting was suspended at the end of two hours.

In Experiments 2, 3 and 4, pressure was first applied to a point several kilograms beyond the final pressure desired. During the following two or three minutes the dissipation of the heat of compression caused the pressure indicated by the gage to slowly diminish.

When the gage reading had become practically constant the pressure was adjusted to the value given in the table and was maintained at this point throughout the experiment.

In Experiment 4, at 750 kg. pressure it was found that, owing to oil leakage at the pump connections, frequent manipulation of the pump was necessary in order to keep up the pressure. The measurements were, therefore, not carried beyond this point.

One of the samples from Expt. 4 became accidentally contaminated after its withdrawal and was not analyzed.

The procedure connected with the taking of the samples was as follows: After the tilting had been suspended the reaction chamber was placed in a vertical position and allowed to stand for fifteen minutes to permit the solid substance to settle. This step is probably not necessary since the slight loosening of the valve which permits the slow expulsion of the liquid would scarcely allow any solid particle to escape.

The bomb was next turned back to the position shown in Fig. 1. This left the end of the outlet tube sufficiently above the surface of the water in the bath to permit the attachment of the weighing bottle which was to receive the sample for analysis.

The outlet tube and the protective rubber tube were thoroughly dried with filter paper and the rubber tube removed.

The weighing bottle was provided, in addition to its glass stopper, with a flat one-hole rubber stopper about 1 cm. in thickness. This rubber stopper was slipped over the end of the outlet tube and the weighing bottle then pushed into the rubber stopper. By this means any loss by evaporation during the withdrawal of the sample was prevented.

The valve was now slightly loosened until the gage began to show a decrease in the pressure indicating the escape of liquid through the valve. The original pressure was at once restored by means of the pump and was kept up during the slow egress of the sample (about 20 drops per minute) into the weighing bottle. When 3-4 cc. of the solution had escaped the valve was tightened, the weighing bottle removed from the rubber stopper and its glass stopper at once inserted and the weighing made.

The analysis of the sample was effected without transferring from the

weighing bottle. The latter was placed in a tall beaker to protect it from the action of steam and the solution evaporated to dryness on the water bath, after which the residue was heated in an air bath for one hour at  $350^{\circ}$ , cooled in a desiccator, and weighed.

TABLE IV.—SOLUBILITY-PRESSURE DATA FOR SODIUM CHLORIDE AT  $25^{\circ}$ .

Expt. No.	Pressure kg. per sq. cm.	Wt. of sample.	% NaCl found.	% water.
1.....	1	4,100	26.44	73.56
	1	3,339	26.44	73.56
2.....	250	3,505	26.58	73.42
	250	3,408	26.58	73.42
3.....	500	3,629	26.76	73.24
	500	2,076	26.68	73.32
4.....	750	4,012	26.82	73.18

The divergence in the results of the analysis of the two samples for Expt. 3 cannot be accounted for.

If the average of the two values (26.72%) be taken, a smooth pressure-solubility curve results for the four points.

The accurate determinations by Andrea of the ordinary solubility (*i. e.*, at atmospheric pressure) of sodium chloride at different temperatures resulted in the values 26.37% and 26.53% for the temperatures  $20^{\circ}$  and  $30^{\circ}$ , respectively. A straight line interpolation for  $25^{\circ}$  gives the value 26.45%, which is one point higher than the result contained in Table IV. The temperature coefficient of solubility  $ds/dt$  calculated from Andrea's data is therefore 0.46/10 or 0.016%.

From the data of Table IV it is seen that an increase in pressure of 249 kg. alters the solubility by only 0.14%.

In both instances it is apparent that a slight variation in the analytical results will produce an immense effect on the ratios  $ds/dt$  and  $dp/ds$ . A satisfactory calculation of the relation  $dA/dt$  as the product  $ds/dt \cdot dp/ds$  ( $V_2 - V_1$ ) is therefore not possible for this substance.

In considering the choice of a solute for which complete thermodynamic data could be readily established, barium hydroxide suggested itself on account of its moderate solubility, its much larger temperature coefficient of solubility than that of NaCl, and the ease and accuracy of its analysis by titration.

Moreover, being an alkaline substance, there is no danger of contamination of the solution through action on the iron.

Data for the heat of solution were found and for the temperature coefficient of solubility and for the specific volume of the solid substance, but owing to the absence of data for the specific volume of its solutions from which the volume change  $V_2 - V_1$  could be calculated, it was not possible to estimate whether its pressure coefficient of solubility were large or small. Instead of first making the density determinations, the measurements with the pressure apparatus were carried out in the manner de-

scribed, except that the samples of solution withdrawn under pressure were titrated with 0.04 *N* hydrochloric acid carefully standardized against anhydrous sodium carbonate and with burets standardized by weight. The solution chamber was charged by preparing a hot solution of barium hydroxide of a concentration twice as great as that possessed by the saturated solution at twenty-five degrees. This hot solution was filtered (to remove carbonate) directly into the bomb and the screw-plug inserted. On cooling, the excess of solid solute separated. The material used was pure crystallized octohydrate and was not analyzed further.

The results are contained in Table V. The equilibrium for atmospheric pressure and for 250 kg. per sq. cm. (245 megabars)<sup>1</sup> was approached from both sides. In Expt. 1, hot water was added to the bath to bring it to a temperature of 30° and the bomb tilted for one-half hour. The bath temperature was then lowered to 25° (where it was maintained by the automatic regulation) and the bomb tilted for three hours at which time the sample was removed.

In Expt. 2 the bath was cooled to 20° and the bomb tilted for one-half hour, after which the temperature was raised to 25° and the tilting continued for three hours as before. The good agreement of the analyses shows that equilibrium was reached in both cases.

In Expts. 3 and 4 the same procedure was followed, except that the tilting at 25° was continued for 2 hours only. The difference in the analyses, although small, is somewhat beyond the probable analytical error and indicates that the tilting had not been quite long enough continued, hence in the subsequent calculation the average value, 8.791, is used.

In Expt. 5 the tilting was continued for 2.5 hours.

TABLE V.—SOLUBILITY OF  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  AT 25° AND VARYING PRESSURES.

Expt. No.	Pressure (megabars).	Wt. of sample.	% hydroxide.	% water.
1.....	1	6.179	8.304	91.696
2.....	1	5.228	8.295	91.705
3.....	245	10.523	8.779	91.221
4.....	245	6.481	8.802	91.198
5.....	490	6.320	9.366	90.634

### The Heat of Solution.

The molar heat of solution of  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  in large amounts of water has been determined by de Forcrand and by Thomsen<sup>2</sup> as  $-14500$  cal. and  $-15210$  cal., respectively. These values correspond to  $-46.0$  cal. and  $-48.2$  cal. per gram of solute. On account of this divergence and the fact that the heat of solution of substances at or near the saturation point may be very different from the values for dilute solutions, two deter-

<sup>1</sup> Megabar =  $10^6$  dynes = 1.02 kilograms per sq. cm.

<sup>2</sup> Landolt-Börnstein Tabellen.

minations were made, the first starting with a solution already 54% saturated and using an amount of solute such as to bring its concentration to 64% saturated. The second determination continued from the latter point and brought the solution to 74% saturated.

The measurements were made in a Richards "adiabatic calorimeter."

During the process of solution the lowering of the temperature within the calorimeter vessel was kept pace with by the addition of colder water to the outside vessel whose contents were kept rapidly stirred.

At no time did the thermometer readings inside and outside differ by more than one-hundredth of a degree.

The initial solution (No. 1) was prepared by diluting a saturated solution and filtering into the calorimeter vessel after which a sample was pipetted out for analysis.

Barium hydroxide (150 g.) was dissolved at 60° and filtered clear into a flask which was then stoppered and allowed to cool. The fine crystals of  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  separating out were quickly filtered in four Gooch crucibles and then rotated rapidly in a centrifuge until no more liquid could be separated. The upper portion of the contents of each crucible, which doubtless contained some carbonate formed during the rotating, was removed with a spatula and the remainder shaken out onto three thicknesses of filter paper and folded up in the latter to form a flat package. This was pressed vigorously between more sheets of filter paper and the contents of the package then transferred to a stoppered bottle. By this means the formation of carbonate was reduced to a negligible amount, as is shown by the fact that a sample of the product, dissolved in previously boiled water, left but a scarcely perceptible turbidity.

A sample of this product was transferred to a weighing bottle, weighed and titrated, with the result that the preparation was found to contain 6% of saturated solution which the treatment with the centrifuge and the filter paper failed to remove.

For each of the two measurements 3 g. of this preparation were roughly weighed into a small thin glass bulb which was sealed and placed in the calorimeter vessel along with the solution. When all was in readiness the bulb was broken by means of a stirrer. The time required for complete solution as indicated by the stationary temperature was eight to ten minutes, moderate stirring being employed.

A sample was withdrawn from the calorimeter vessel by means of a 10 cc. pipet, weighed and titrated. From the result of this titration the total increase in the octohydrate content of the solution was computed. From this amount was deducted the weight of octohydrate in the 6% of saturated solution which had been present in the sealed bulb and which had had no appreciable thermal effect. This correction amounts to  $6\% \times 8.3\% = 0.5\%$ .



The remainder gives the amount of solid octohydrate which had actually passed into solution during the calorimeter measurement.

These figures are contained in the fifth column of the following table:

TABLE V.

Solution No.	% hydrate.	Degree of saturation.	Grams of sol. used.	Grams solid hydrate dissolved.	Temperature change
1.....	4.502	54%	360	2.948	—0.381°
2.....	5.280	64%	352	3.228	—0.437°
3.....	6.155	74%	...	.....	.....

The heat of solution per gram of solid hydrate added in bringing a 54% saturated solution to 64% saturation as calculated from these data is 48.3 calories and in bringing the latter solution to 74% saturation, 49.1 calories, account being taken of the heat capacity (10 cal.) of the calorimeter, stirrer, glass fragments, etc. A straight-line extrapolation gives the value 51.2 cal. for the heat of solution at the saturation point.

The heat capacity of the solutions may vary from that of water by 1-2%, but in the absence of any data no account could be taken of this possible difference.

#### The Volume Change.

A simple and accurate means of determining the volume change was suggested by the observations made in the course of the previous work that barium hydroxide solutions could be easily kept at a high degree of supersaturation. From this fact it appeared that a dilatometer measurement in which a supersaturated solution of known composition should be precipitated by inoculation would yield the desired value.

The successful use of mercury as a stirrer in the pressure-solubility experiments led to its adoption for the same purpose in hastening the approach to equilibrium in the dilatometer.

Fifty cc. of mercury were placed in a three and one-half liter round-bottomed flask whose neck was constricted at the opening to such a diameter as would accommodate a No. 1 one-hole rubber stopper. Through the stopper passed a glass tube of 5 mm. bore graduated in tenths of cubic centimeters. As the graduation marks were about six millimeters apart, hundredths of cubic centimeters could be readily calculated.

The octohydrate (400 g.) was dissolved in four liters of water by heating and the warm solution filtered into a four-liter flask which was stoppered and placed in the thermostat of 25° for several hours. The solution, which was calculated to be about 10% supersaturated at this temperature, remained perfectly clear. A sample (about 10 cc.) was pipetted out, weighed, and titrated and found to contain 9.199% of octohydrate.

The dilatometer flask containing the mercury, together with the rubber stopper and graduated tube, were counterpoised on a balance and the flask filled to the top with the supersaturated solution.

The rubber stopper was now inserted, causing a little of the solution to be expelled through the hole. The volumetric tube was then pushed through the stopper, the displacement of the liquid by the tube thereby raising the level to a convenient point on the scale.

The whole apparatus was weighed and found to contain 3540 g. of solution.

A small soda-lime tube was attached to the upper end of the volumetric tube and the flask immersed in the thermostat bath for half a day. During the last two hours of this period readings of the level in the tube were made and after each reading the mercury was swirled about in the flask.

The meniscus reading remained unchanged during the two hours and the solution entirely clear.

A minute particle of solid octohydrate about one-half millimeter in diameter was taken with a forceps and dropped down the tube and was seen to fall through the solution and rest on the bright mercury surface at the bottom of the flask. Flakes of octohydrate soon began to appear and the solution level to rise in the graduated tube. The process was hastened by agitating the mercury every few minutes.

At the end of six hours a large deposit of octohydrate had separated and an increase in volume of 1.28 cc. had taken place. No further rise in the meniscus level could be observed after an additional half hour.

Since the stirring had been only for a few seconds at intervals of from three to six minutes instead of being continuous as in the pressure-bomb experiments, it was not to be supposed that complete equilibrium had been established. The fact that no measurable increase in volume had occurred during half an hour indicated, however, that a sample of the solution could be safely removed for analysis.

The stopper and tube were accordingly removed and a sample drawn into a 10 cc. pipet, transferred to a weighing bottle, and weighed.

Although the solid octohydrate settles quickly, leaving the solution clear, the precaution was taken of attaching to the pipet a 5 cm. piece of glass tubing, constricted in the middle and packed below the constriction with a plug of cotton.

The titration analysis of the sample showed 8.487% of  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ .

The total of the solid phase which had separated was accordingly

$$3540(0.09199 - 0.08487) = 25.205 \text{ grams,}$$

$$\text{and the specific volume change } (V_2 - V_1) \text{ was } \frac{1.28}{25.205} = 0.0508.$$

#### The Temperature Coefficient of Solubility.

This value was calculated from the solubility data of Rosenstühl and Rühlmann.<sup>1</sup> This table gives the percentage of BaO in the saturated

<sup>1</sup> Taken from the Landolt-Börnstein tables, 1912, p. 459.

solution for temperatures at intervals of  $10^{\circ}$ . The following table shows these values and equivalent values for  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ :

	BaO.	$\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ .
$10^{\circ}$	2.17%	4.46%
$20^{\circ}$	3.36%	6.91%
$30^{\circ}$	4.75%	9.77%
$40^{\circ}$	6.85%	14.09%

When these four points are plotted and a smooth curve drawn, the curve-reading for the solubility at  $25^{\circ}$  is 8.30%, agreeing with the value obtained by direct measurement (Table V).

Hence the Rosenstühl-Rühlmann data may serve as a basis for the calculation,

$$\frac{ds}{dt} = \frac{9.77\% - 6.91\%}{10^{\circ}} = 0.288\%.$$

The application of the complete data to the equation

$$T \frac{(p_2 - p_1)(v_2 - v_1)}{t_2 - t_1} = Q$$

gives for the left-hand side

$$298 \times 0.288 \times \frac{244}{0.491} \times 10^6 \times 0.0508 = 2.16 \times 10^9$$

and for the right-hand side

$$51.2 \times 4.189 \times 10^7 = 2.14 \times 10^9.$$

The agreement is seen to be excellent.

The writer wishes to acknowledge his thanks to Prof. T. W. Richards, of Harvard University, for valuable advice and assistance in the devising of the pressure bomb employed in this investigation. This apparatus is owned by the Carnegie Institution of Washington and is now being used for other work under the auspices of the Institution.

COLUMBIA, MISSOURI.

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[CONTRIBUTION FROM KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

## STUDIES ON THE COBALTAMMINES. I.

### VARIOUS IONIZATION TYPES AS DETERMINED BY THE FREEZING-POINT LOWERING IN AQUEOUS SOLUTION, TOGETHER WITH CONDUCTANCE MEASUREMENTS.<sup>1</sup>

BY WILLIAM D. HARKINS, R. E. HALL AND W. A. ROBERTS.

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The present investigation was undertaken as a starting point in the study of the structure of the cobaltammines. The first point necessary

<sup>1</sup> The temperature readings were taken to one-twenty thousandth of a degree by means of a 50 couple thermoelement, and a double combination potentiometer specially designed for this work by Dr. W. P. White, and we wish to express our indebtedness to him for this aid.

to establish was the type of salt for the different groups under which the cobaltammines may be classified, *i. e.*, the number of ions which they give in aqueous solution. That it is essential that such an investigation should be undertaken, is indicated by the great divergence, amounting to 100% or more, between the results of various investigators in this field, such as that which exists between the results on freezing-point lowering as obtained by E. Petersen<sup>1</sup> and by Werner and Herty,<sup>2</sup> and by the discrepancies which exist between the various results obtained by any one individual investigator.

Petersen criticized the empirical conductivity comparison method employed by Werner for determining the number of ions from his conductivity data, and proposed, by substituting for  $\gamma$  in the Equation  $i = 1 + (n - 1)\gamma$ , the value obtained for it from the conductivity ratio  $\lambda/\lambda_0$ , to determine  $n$  by giving it different integral values (1, 2, 3, etc.), and finding which one would fit for the value of  $i$ , determined from freezing-point depressions. This work was done during the latter part of the controversy between Werner and Jørgensen, and the materials for it were furnished by the latter. Petersen used as his  $\lambda_0$  merely the value of  $\lambda$  derived from his conductivity measurements at the lowest concentration used (1 mol of salt to 3200 liters of water), and did not extrapolate his results to obtain the real  $\lambda_0$ . With the exception of some three of the salts, he was unfortunate, too, in his choice of compounds, as he used substances which hydrolyze quite readily, and were therefore of little value in determining the point in question. About four years later, Werner and Herty replied to Petersen, severely criticizing his work, and gave freezing-point data on a few salts. Table I summarizes the results on the only salt on which both Petersen and Werner and Herty give freezing-point data.

TABLE I.—SUMMARY OF PETERSEN'S AND WERNER AND HERTY'S FREEZING-POINT DATA ON CROCEO COBALTAMMINE.

Petersen. Dinitrotetrammine cobalt nitrate.				Werner and Herty. Dinitrotetrammine cobalt chloride.			
Conc. N <sup>3</sup> X 10 <sup>3</sup> .	Depression, $\Delta t$ .	$\Delta t/N$	$i$ .	Conc. N X 10 <sup>3</sup> .	Depression, $\Delta t$ .	$\Delta t/N$ .	$i$ .
5.0	0.030	6.00	3.23	4.35	0.015	3.45	1.74
10.0	0.058	5.80	3.12	4.72	0.017	3.60	1.82

While their results on conductivity were in fair agreement, the disparity in the freezing-point measurements was so great that Werner's criticisms on Petersen's method, suggesting, as the cause for the difference, an error in determining the real zero on his Beckmann thermometer because of solubility of the freezing-point vessel in the water, can really

<sup>1</sup> *Z. physik. Chem.*, **22**, 310 (1897); *Ibid.*, **39**, 249 (1902).

<sup>2</sup> *Ibid.*, **38**, 331 (1901).

<sup>3</sup> N represents the equivalent concentration per 1000 g. of water and  $\Delta t$  the lowering of the freezing point.

serve as no explanation at all. He very justly pointed to the fact that, owing to the small solubility of the salts, the difficulties encountered in freezing-point determinations would lead to uncertain conclusions. When it is considered that the limit of accuracy of the ordinary Beckmann thermometer is  $0.001^{\circ}$ —and the ordinary Beckmann apparatus was evidently used by both Werner and Petersen—and notes the temperature depressions recorded in Table I, it is not difficult to account for a difference of 5–10% in their measurements. But the disparity amounts to almost 100%—great enough so that while Werner interpreted the croceo salt as one giving two ions in aqueous solution, Petersen designated it a tetraionic salt.

The method of determining freezing-point lowerings by the use of a fifty junction copper-constantan thermoelement<sup>1</sup> can be applied with accuracy to low concentrations of solution, and the use of the interferometer for analysis, while interfered with by the color of the cobalt-ammines, permits the determination of the concentration of the equilibrium mixture of these complex salts. We therefore decided to determine the freezing-point lowerings of a few of them, choosing for our work those which showed the least tendency to instability in aqueous solution. The well-known series described by Werner<sup>2</sup> meets this requirement very well, and includes salts of the different types of ionization.

We therefore prepared the following salts:

Hexammine (luteo) cobalt chloride.....	$\text{Co}(\text{NH}_3)_6\text{Cl}_3$
Nitropentammine (xantho) cobalt chloride.....	$(\text{NO}_2)\text{Co}(\text{NH}_3)_5\text{Cl}_2$
Chloropentammine (purpureo) cobalt chloride.....	$\text{ClCo}(\text{NH}_3)_5\text{Cl}_2$
Dinitrotetrammine (croceo) cobalt chloride.....	$(\text{NO}_2)_2\text{Co}(\text{NH}_3)_4\text{Cl}$
Dinitrotetrammine (flavo) cobalt nitrate.....	$(\text{NO}_2)_2\text{Co}(\text{NH}_3)_4\text{NO}_3$
Trinitrotri­ammine cobalt.....	$(\text{NO}_2)_3\text{Co}(\text{NH}_3)_3$
Potassium tetranitrodiammine cobaltate (Erdmann's salt).....	$(\text{NO}_2)_4\text{Co}(\text{NH}_3)_2\text{K}$
Ammonium tetranitrodiammine cobaltate.....	$(\text{NO}_2)_4\text{Co}(\text{NH}_3)_2\text{NH}_4$
Sodium cobaltic nitrite.....	$(\text{NO}_2)_6\text{CoNa}_3$

While some of the salts of this series are rather unstable and hydrolyze readily at higher temperatures, at zero degrees no trouble was experienced, except with dinitrotetrammine cobalt chloride, and with this only on exposure to bright light, and with sodium cobaltic nitrite. To dispense with any error from hydrolysis, all analyses of the equilibrium mixtures were made on the same day as, and immediately following, the determination of the freezing-point lowerings. Only rather limited data on these salts could be obtained, owing to their slight solubility. However, determinations could be made at a sufficient number of concentrations to

<sup>1</sup> Adams, *THIS JOURNAL*, 37, 481 (1915).

<sup>2</sup> *Z. physik. Chem.*, 14, 506 (1894); "New Ideas on Inorganic Chemistry" (English edition), pp. 40, 41, 157, 158; *Ber.*, 40, 26 (1907).

plot the curve for  $\Delta t/N$  against a function of the concentration, and to permit comparison of this with the curve of some simple salt.

### Preparation of the Salts.

**Chloropentammine Cobaltic Chloride**,  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}$ , was prepared by Sørensen's method.<sup>1</sup> 20 g. of cobalt carbonate were dissolved in the least amount of 1:1 HCl possible. The filtered and cooled solution was added to a mixture of 250 cc. of concentrated ammonia solution and 50 g. of  $(\text{NH}_4)_2\text{CO}_3$  dissolved in 250 cc. of water. This was then put in a large flask and a rapid stream of air passed through it for three hours. 150 grams of  $\text{NH}_4\text{Cl}$  were added and the solution evaporated on a water bath until it became a crystal pulp. The  $(\text{NH}_4)_2\text{CO}_3$  was decomposed by HCl and the solution made alkaline by the addition of 10 cc. excess  $\text{NH}_4\text{OH}$ . Complete precipitation of the salt was accomplished by the addition of 300 cc. of concentrated HCl. After heating on the water bath for an hour to decompose any aquopentammine the salt was collected on a filter and washed with dilute HCl.

For purification the salt was dissolved in a weak solution of ammonia by heating on a water bath. It was precipitated by concentrated HCl heated on the water bath and filtered. This process was repeated four times. After final washing with dilute HCl, redistilled alcohol and ether it was dried in a desiccator and heated to constant weight at forty degrees in an air bath. Scarcely any loss of weight occurred during the heating. An analysis was made by treating a sample with  $\text{H}_2\text{SO}_4$  and weighing as  $\text{CoSO}_4$ , and gave 0.2113 g. of  $\text{CoSO}_4$ . The amount calculated from the formula was 0.2115.

**Hexammine Cobaltic Chloride**,  $\text{Co}(\text{NH}_3)_6\text{Cl}_2$ , was prepared by Jörgensen's method.<sup>2</sup> 10 grams of chloropentammine cobaltic chloride, 100 cc. of 20% ammonia and 8 grams  $\text{NH}_4\text{Cl}$  were placed in a pressure flask which held about 110 cc. The flask was put in a water bath and heated with shaking every hour until no trace of the pentammine could be seen. This required on the average about five hours. After cooling the contents of the flask were poured into an open vessel and the ammonia removed by suction in a vacuum desiccator. The flask contained mostly hexammine with a little chloropentammine and aquopentammine. When the ammonia had been removed, the mixture was diluted to 300 cc. and 50 cc. concentrated HCl were added. It was heated on the water bath for an hour, 0.5 of its volume of concentrated HCl was then added, and the solution cooled and filtered. For purification the hexammine, which is rather soluble in water, was removed from the pentammine by extracting with cold water. The reprecipitation was carried out as above. It was washed and dried in the same way as the pentammine.

**Nitropentammine Cobaltic Chloride**,  $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$ , was prepared as recommended by Jörgensen. 20 grams of chloropentammine cobaltic chloride were dissolved in 200 cc.  $\text{H}_2\text{O}$  and 50 cc. of 10% ammonia on the water bath. The solution was filtered, acidified with HCl and then heated for some time with 25 grams  $\text{NaNO}_2$ . Complete precipitation was accomplished by the addition of 250 cc. concentrated HCl. It was filtered, washed many times with dilute HCl, alcohol and ether and then dried.

**Dinitrotetrammine (croceo) Cobalt Chloride**.—The method recommended by Jörgensen<sup>2</sup> was followed. Cobalt carbonate was dissolved in the requisite amount of hydrochloric acid; ammonium chloride, sodium nitrite, and ammonium hydroxide were added, and air was drawn through the solution for several hours. The precipitated salt was separated on a Hirsch funnel, and washed repeatedly to remove the small quantities of xantho chloride contaminating it, until no test for the xantho salt was

<sup>1</sup> *Z. anorg. Chem.*, **5**, 369 (1894).

<sup>2</sup> *Ibid.*, **17**, 455 (1898).

given by ammonium oxalate. To convert this mixture of croceo chloride and nitrate to the pure chloride, it was dissolved in water weakly acidified with acetic acid, and a large amount of ammonium chloride was added; the solution was cooled, and allowed to stand for a few hours. The salt which separated was washed thoroughly first with water, and finally with 90% alcohol. It was dried, and recrystallized from water very weakly acidified with acetic acid. Although Jörgensen recommends recrystallization without acid, it was found impossible to do this without some hydrolysis, and the consequent precipitation of a varying amount of an oxide of cobalt. 150 g. of the pure salt were prepared. The air-dry salt was brought to constant weight at 80°.

**Dinitrotetrammine (flavo) Cobalt Nitrate.**<sup>1</sup>—The first preparation was carbonato-tetrammine cobalt sulfate,<sup>2</sup> which was made by dissolving cobalt carbonate in the requisite amount of sulfuric acid, adding ammonium carbonate and ammonium hydroxide, oxidizing by drawing air through the solution for a few hours, concentrating on the water bath with frequent addition of a little ammonium carbonate, cooling to 0°, and filtering on a platinum cone. This material was then converted into the flavo salt by dissolving in dilute nitric acid, adding sodium nitrite, heating on the water bath for a few minutes, cooling, and leaving in the ice chest for several hours. The acid flavo nitrate which separated was washed with dilute nitric acid, and changed to the neutral salt by further washing with alcohol to neutral reaction. The salt was recrystallized from hot water, very weakly acidified with acetic acid, and was separated on a platinum cone. 140 g. of the pure salt were prepared. The air-dry salt was brought to constant weight at 50°.

**Trinitrotetrammine Cobalt.**<sup>3</sup>—Cobalt carbonate was dissolved in just the requisite amount of hydrochloric acid, and the solution was poured into a solution containing ammonium chloride, sodium nitrite, and ammonium hydroxide. The cobalt was oxidized by drawing air through the mixture for a few hours. After standing for a week in open dishes, the solution had lost its odor of ammonia and had decreased in volume by half. The solid material which had separated consisted of a yellow slime and dark brown crystals. To remove all traces of chloride, repeated washing was necessary, and it was found expedient to do this by decantation, as the crystals were practically chloride-free. This salt was finally dissolved in boiling water containing a little acetic acid, and crystallized by cooling to 0°. The air-dry salt was brought to constant weight at 80°. An analysis for cobalt showed 23.76%; theoretical, 23.77%.

**Potassium Tetranitrodiammine Cobaltate.**<sup>4</sup>—Cobalt carbonate was converted into the chloride, ammonium chloride was dissolved in the solution, the mixture heated to 50°, and a very concentrated solution of potassium nitrite at the same temperature added. The temperature was maintained at 50° for half an hour. After some hours, a fine yellow powder and dark brown crystals had separated from the solution. Most of the powder was removed by decanting off the original solution, and washing the crystals with cold water in the same manner; the remainder, by dissolving the crystals in hot water, and filtering off the practically insoluble powder. The salt obtained on cooling the solution was recrystallized from pure water, and brought to constant weight at 50°. An analysis for cobalt showed 18.61%; theoretical, 18.65%.

**Ammonium Tetranitrodiammine Cobaltate.**—The procedure was similar to that used in the preparation of the preceding salt, with the exception that sodium nitrite was used in place of potassium nitrite. An analysis for cobalt showed 20.16%; theoretical, 19.98%.

<sup>1</sup> *Z. anorg. Chem.*, **17**, 455 (1898).

<sup>2</sup> *Ibid.*, **2**, 282 (1892).

<sup>3</sup> Jörgensen, *Loc. cit.*

<sup>4</sup> *J. prakt. Chem.*, [2] **23**, 249 (1881).

**Sodium Cobalt Nitrite.**<sup>1</sup>—The method recommended by Biltz was followed in this preparation. The air-dry salt was brought to constant weight at 50°. An analysis made by weighing the sodium and cobalt as sulfates showed for the cobalt 14.03%. This salt is described in the literature<sup>2</sup> as one of varying amounts of water of hydration. On the basis of the formula  $(\text{NO}_2)_6\text{CoNa}_3$ , the theoretical percentage of cobalt is 14.60; for  $(\text{NO}_2)_6\text{CoNa}_3 \cdot \text{H}_2\text{O}$ , 13.97. The freezing-point data were figured on the basis of the latter formula. However, the difference in values obtained, using one formula or the other, is of little significance, as the decomposability of the salt in aqueous solutions renders any determination at best merely an approximation.

### Freezing-Point Data.

The method followed in this work was the same as will be described in a later paper. On account of the color of the solutions, the analysis with the interferometer proved rather troublesome, and probably a

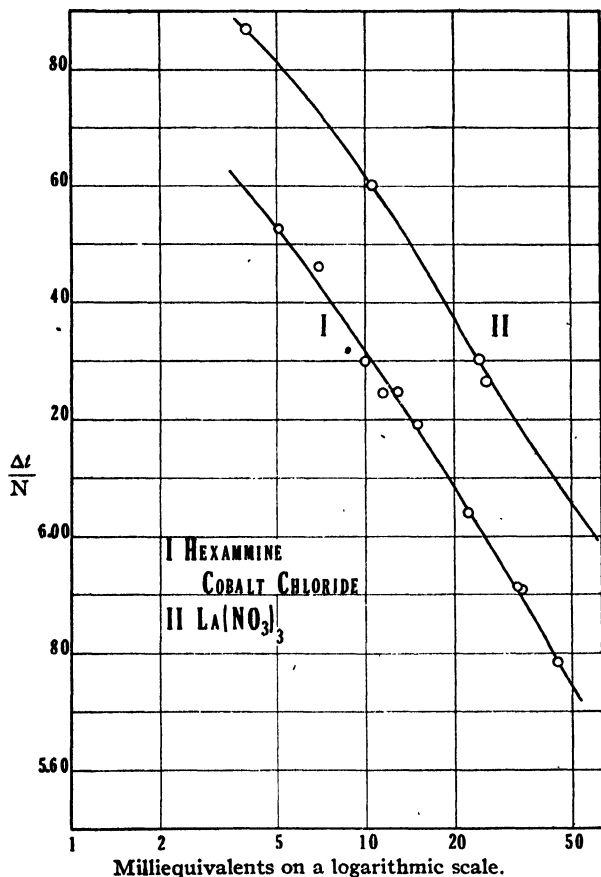


Fig. 1.—Values of  $\Delta t/N$  for the freezing-point lowerings of hexamine (luteo) cobalt chloride and of lanthanum nitrate.

method based on conductivity measurements would be even more satisfactory. The difficulties experienced in the analysis account largely for the slight irregularities of the individual points on the curves as plotted. All data are calculated on the basis of weight normality.

**Hexamine Cobalt Chloride.**—This is one of the most stable salts of the series. Table II comprises the data on this salt, and the values obtained by Werner. Table III includes our data at rounded concentrations, the corresponding  $i$  values for lanthanum nitrate, and the apparent ionization as obtained from the

<sup>1</sup> Biltz, "Laboratory Methods of Inorganic Chemistry," 1909, p. 149.

<sup>2</sup> Moissan, *Chim. Minerale*, 4, 206 (1905), and the references listed.



conductivity measurements of Roberts at  $0^{\circ}$ . The latter are calculated on the basis of volume normality; but the concentrations are small enough so that very little change would be made by recalculating on the basis of weight normality. Fig. 1 shows the curve of  $\Delta t/N$  plotted against the logarithm of the concentration, and the corresponding curve for lanthanum nitrate. Fig. 2 plots our values on a smaller scale, in order to include Werner and Herty's data. The freezing-point lowerings, are smaller throughout than those shown by lanthanum nitrate. However, the agreement is such as to leave no doubt that the

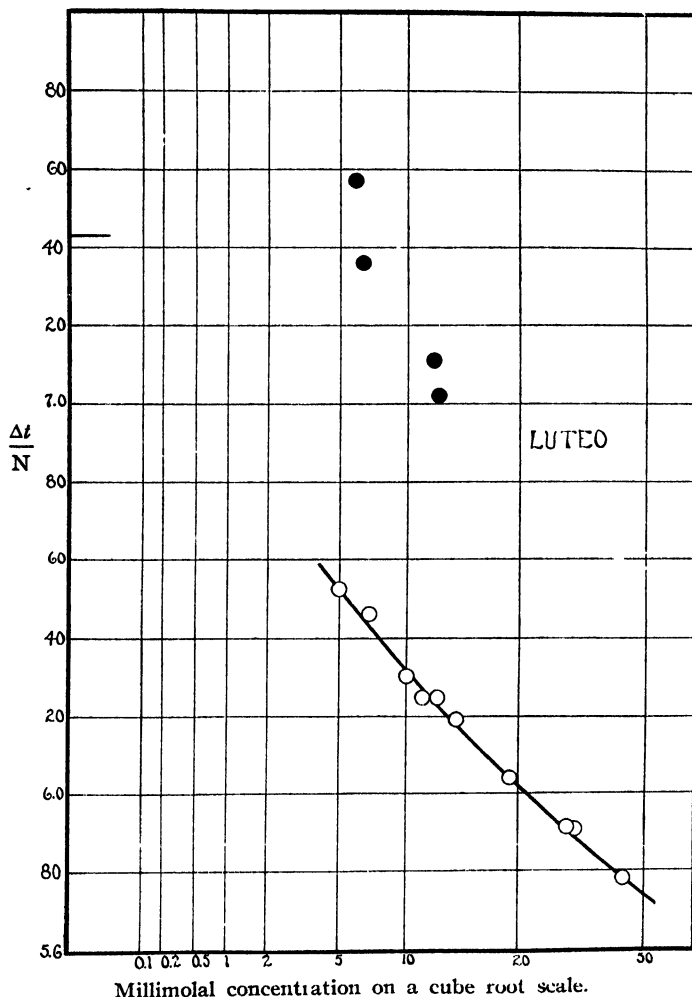


Fig. 2.—Values of  $\Delta t/N$  from the freezing-point lowerings of solutions of hexammine (luteo) cobalt chloride, a tri-univalent salt. The black circles represent the results of Werner and Herty.

hexammine salt is of the same type as the lanthanum nitrate—a tetraionic salt.

TABLE II.—SUMMARY OF THE DATA TAKEN ON HEXAMMINE COBALT CHLORIDE, AND OF WERNER AND HERTY'S VALUES.

Conc. N $\times 10^3$ .	Equivalents (10) <sup>3</sup> .	Depression, $\Delta t$ .	$\Delta t/N$ .	
1.69	5.05	0.0110 <sub>1</sub>	6.527	
2.31	6.92	0.0149 <sub>0</sub>	6.461	
3.35	10.05	0.0211 <sub>0</sub>	6.300	
3.84	11.53	0.0240 <sub>6</sub>	6.247	
4.31	12.92	0.0269 <sub>2</sub>	6.248	
5.02	15.05	0.0310 <sub>7</sub>	6.191	
7.43	22.30	0.0449 <sub>0</sub>	6.040	
10.89	32.67	0.0644 <sub>3</sub>	5.913	
11.29	33.87	0.0667 <sub>2</sub>	5.909	
14.95	44.85	0.0864 <sub>6</sub>	5.783	
Werner and Herty. <sup>1</sup>				
1.98	5.94	0.0112	7.57	<i>i.</i> 4.08
2.12	6.36	0.0166	7.36	3.96
4.15	12.44	0.0295	7.11	3.83
4.27	12.82	0.03	7.02	3.78

TABLE III.—DATA ON HEXAMMINE COBALT CHLORIDE AT ROUNDED CONCENTRATIONS.

Conc. Equivalents (10) <sup>3</sup> .	$\Delta t/N$ .	<i>i.</i>		$\gamma$ .	
		Hexammine.	La(NO <sub>3</sub> ) <sub>3</sub> .	F.-P. L.	(Roberts) Cond.
5	6.527	3.513	3.666	83.8	82.8
10	6.317	3.399	3.562	80.0	78.7
20	6.085	3.275	3.429	75.8	73.6
50	5.741	3.089	3.261	69.6	65.2

**Nitropentammine and Chloropentammine Cobalt Chloride.**—Fig 3 shows the curves for these salts in relation to the curve of cobalt chloride. It will be seen that they are very much steeper over the range possible to investigate than that of the cobalt chloride. The points taken by Werner and Herty on the xantho salt are also plotted. Table IV collects our data, and that of Werner and Herty; Table V includes the data at rounded concentrations, the *i* values of cobalt chloride, and the ionization values determined by Roberts' conductivity measurements at 0°. The salts, especially the purpureo, show high ionization values. Evidently they are quite comparable to cobalt chloride, and are therefore of the three ion type.

**Dinitrotetrammine Cobalt Salts. Croceo Chloride and Flavo Nitrate.**—Fig. 4 plots the curves of these salts, shows the points determined by Werner and Herty, and gives also the curve for potassium iodate, as a representative di-ionic salt. The difference in the slope of the curves for the croceo and flavo salts is only slightly greater than that between potassium chloride and potassium nitrate (Fig. 5 of the following paper).

<sup>1</sup> The data given by Werner and Herty, *Z. physik. Chem.*, 38, 352 (1901), have been recalculated on the basis of 1.858 for the molal lowering.

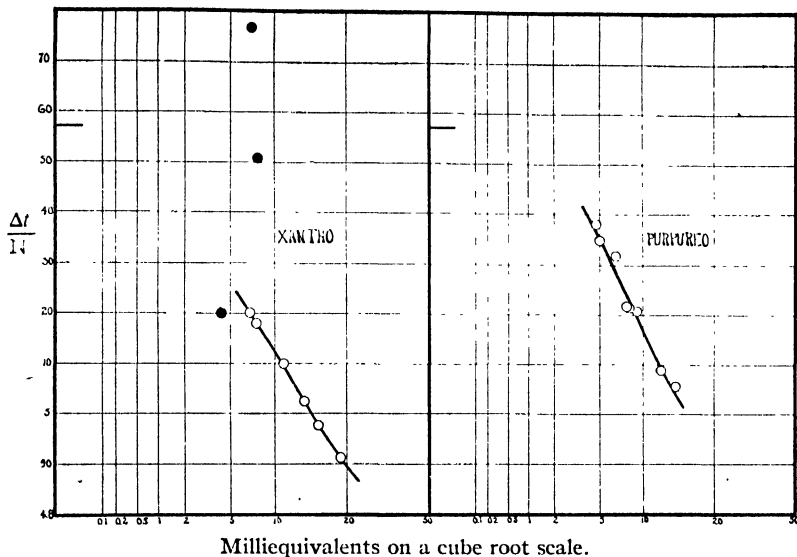


Fig. 3.—Values of  $\Delta t/N$  for nitropentammine (xantho) cobalt chloride and chloropentammine (purpureo) cobalt chloride. The black circles give the results of Werner and Herty.

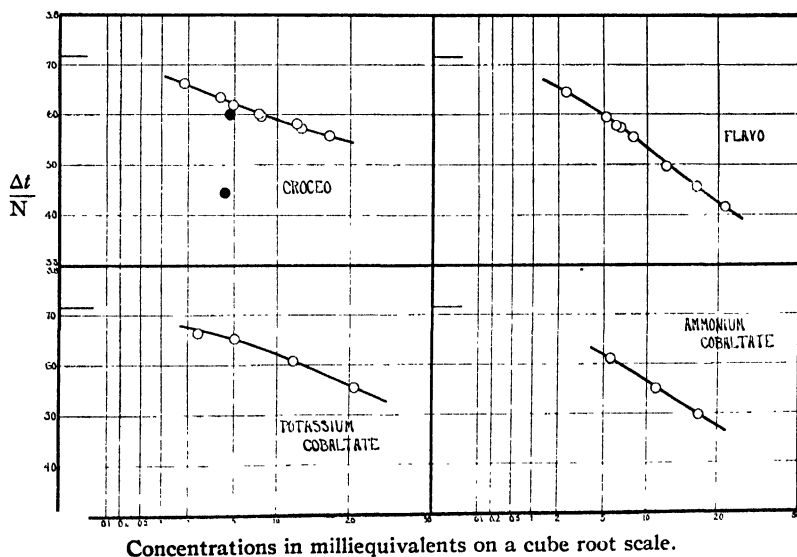


Fig. 4.—Values of  $\Delta t/N$  from the freezing-point lowerings of dinitrotetrammine (croceo) cobalt chloride, dinitrotetrammine (flavo) cobalt nitrate, two isomeric compounds, and of potassium and ammonium tetranitrodiammine cobaltates, a series of univalent salts. The black circles give the values of Werner and Herty. The bottom line in each of these four plots represents a value of 3.30 for  $\Delta t/N$ .

TABLE IV.—SUMMARY OF THE DATA TAKEN ON XANTHO AND PURPUREO COBALT CHLORIDES, AND OF WERNER AND HERTY'S VALUES.

Concentration. $N \times 10^3$ .	Equivalents (10) <sup>3</sup> .	F.-P. depression, $\Delta t$ .	$\Delta t/N$ .	
Xantho Cobalt Chloride.				
1.54	3.09	0.00803	5.201	
3.54	7.08	0.01841	5.203	
3.86	7.72	0.02000	5.180	
5.71	11.41	0.02910	5.102	
7.45	14.89	0.03740	5.023	
8.71	17.41	0.04330	4.976	
10.92	21.83	0.05363	4.912	
Werner and Herty.				
2.12	4.23	0.011	5.20	i.
3.64	7.28	0.021	5.77	2.63
4.08	8.16	0.0225	5.51	2.92
Purpureo Cobalt Chloride.				
2.45	4.90	0.01319	5.380	
2.49	4.97	0.01330	5.350	
3.40	6.80	0.01809	5.318	
3.98	7.96	0.02075	5.216	
4.16	8.33	0.02171	5.215	
4.62	9.24	0.02405	5.207	
6.44	12.88	0.03277	5.088	
7.76	15.51	0.03931	5.056	

TABLE V.—DATA ON XANTHO AND PURPUREO COBALT CHLORIDES AT ROUNDED CONCENTRATIONS.

Concentration. Equiv. (10) <sup>3</sup> .	$\Delta t/N$ .	i.		$\gamma$ .	
		Cobaltamine.	CoCl <sub>2</sub> .	F.-P. D.	(Roberts) Cond.
Xantho Cobalt Chloride.					
5	5.263	2.832	2.840	91.6	91.2
10	5.127	2.760	2.796	88.0	87.8
20	4.939	2.658	2.749	82.9	....
Purpureo Cobalt Chloride.					
2	5.44	2.93		96.0	95.6
5	5.357	2.883		94.2	92.8
10	5.178	2.787		89.4	89.3

TABLE III.—DATA TAKEN ON CROCEO AND FLAVO COBALT SALTS, AND ALSO WERNER AND HERTY'S AND PETERSEN'S VALUES.

Concentration.		F.-P. depression.	
$N \times 10^3$ .	Equivalents (10) <sup>3</sup> .	$\Delta t$ .	$\Delta t/N$ .
	Croceo Cobalt Chloride.		
1.82	1.82	0.00665	3.661
3.92	3.92	0.01426	3.635
4.88	4.88	0.01766	3.619
6.63	6.63	0.02399	3.621
7.62	7.62	0.02745	3.602
7.93	7.93	0.02852	3.596
12.86	12.86	0.04607	3.583
13.70	13.70	0.04894	3.573
18.79	18.79	0.06687	3.559

TABLE VI (continued).

Concentration.		F-P. depression, $\Delta t$ .	$\Delta t/N$ .	$i$ .
$N \times 10^3$ .	Equivalents (10) <sup>1</sup> .			
Werner and Herty.				
4.35	4.35	0.015	3.45	1.74
4.72	4.72	0.017	3.60	1.82
Flavo Cobalt Nitrate.				
2.35	2.35	0.00857	3.643	
4.40	4.40	0.01596	3.630	
5.14	5.14	0.01846	3.594	
6.17	6.17	0.02208	3.579	
6.67	6.67	0.02383	3.575	
8.25	8.25	0.02931	3.555	
12.86	12.86	0.04495	3.495	
18.57	18.57	0.06421	3.457	
25.00	25.00	0.08539	3.416	
Petersen's Data.				
5	5	0.035	7.00	3.77
10	10	0.066	6.60	3.55
20	20	0.123	6.15	3.31

TABLE VII.—DATA ON THE CROCEO AND FLAVO SALTS AS COMPARED WITH  $KIO_3$  AND  $KNO_3$  AT ROUNDED CONCENTRATIONS.

Concentration. Equiv. (10) <sup>2</sup> .	$\Delta t/N$ .	<i>i</i> .		$\gamma$ .	
		Cobaltamine.	KIO <sub>3</sub> . <sup>1</sup>	From F-P. D.	(Roberts) from conductivity.
Croceo Cobalt Chloride.					
2	3.66	1.97	1.94	97.0	95.4
5	3.622	1.949	1.929	94.9	93.2
10	3.590	1.932	1.912	93.2	90.7
20	3.556	1.914	1.889	91.4	....
Flavo Cobalt Nitrate. KNO <sub>3</sub> .					
2	3.65	1.964	1.967	96.4	96.6
5	3.595	1.935	1.958	93.5	93.8
10	3.531	1.900	1.937	90.0	91.2
20	3.446	1.855	1.908	85.5	....

**Croceo and Flavo Salts.**—These interesting isomeric inorganic salts are evidently di-ionic, and correspond very closely to the ordinary di-ionic salts in their freezing-point lowerings.

**Trinitrotri-amine Cobalt.**—The insolubility of this salt renders accurate freezing-point determinations very difficult. The greatest temperature depression noted, as shown in Table VIII, was a little more than  $0.005^\circ$ . This, in conjunction with the difficulty of analyzing the equilibrium mixture, as mentioned above, serves to explain the discrepancies in the  $i$  values given in the table. It is interesting to note that this is the only case in which our values are in agreement with those of Petersen. So far as can be shown by freezing-point measurements, the salt is a non-electrolyte.

<sup>1</sup> L. H. Adams, *THIS JOURNAL*, 37, 495 (1915).

TABLE VIII.—SUMMARY OF THE DATA TAKEN ON TRINITROTRIAMMINE COBALT AND PETERSEN'S VALUES.

Concentration, $N \times 10^3$ .	F.-P. depression, $\Delta t$ .	$\Delta t/N$ .	$i$ .
1.83	0.00351	1.92	1.03
1.86	0.00346	1.86	1.00
2.13	0.00394	1.85	1.00
2.14	0.00367	1.72	0.93
2.74	0.00489	1.79	0.96
2.97	0.00532	1.79	0.96
Petersen's Values.			
4.35	0.008	1.84	0.99
4.17	0.0085	2.04	1.10

**Potassium and Ammonium Tetranitrodiammine Cobaltates.**—Fig. 4 and Tables IX and X collect the data on these salts. They are highly ionized, and evidently di-ionic.

TABLE IX.—SUMMARY OF THE DATA TAKEN ON POTASSIUM AND AMMONIUM COBALTATES.

Concentration, $N \times 10^3$ .	Equivalents (10) <sup>3</sup> .	F.-P. depression, $\Delta t$ .	$\Delta t/N$ .
Potassium Tetranitrodiammine Cobaltate.			
2.54	2.54	0.00931	3.665
5.15	5.15	0.01883	3.651
12.36	12.36	0.04463	3.609
24.90	24.90	0.08847	3.554
Ammonium Tetranitrodiammine Cobaltate.			
2.38	2.38	0.00862	3.625
5.74	5.74	0.02075	3.612
11.54	11.54	0.04096	3.550
19.21	19.21	0.06714	3.495

TABLE X.—DATA AT ROUNDED CONCENTRATIONS FOR POTASSIUM AND AMMONIUM COBALTATES, AND FOR POTASSIUM IODATE USED FOR COMPARISON.

Concentration. Equiv. (10) <sup>3</sup> .	$\Delta t/N$ .	<i>i</i> .		F.-P. D.
		Cobaltamine.	KIO <sub>3</sub> .	
		Potassium Tetranitrodiammine	Cobaltate.	
2	3.68	1.98	1.94	98.0
5	3.652	1.965	1.929	96.5
10	3.620	1.948	1.912	94.8
20	3.573	1.923	1.889	92.3
		Ammonium Tetranitrodiammine	Cobaltate.	
2	3.66	1.97		97.0
5	3.620	1.948		94.8
10	3.564	1.918		91.8
20	3.492	1.879		87.9

**Sodium Cobaltic Nitrite.**—The instability of this salt in aqueous solution rendered any accurate determination of the freezing-point depression an impossibility. The salt was dissolved and introduced into the freezing-point jars as quickly as possible, and the temperature depression noted as soon as equilibrium was attained. With the introduction of the salt, the temperature fell rapidly for a short time, and from then on, slowly

but continuously. The attainment of equilibrium evidently occurred when this slow change commenced, and the temperature reading was taken at this point. The concentration of the freezing-point mixture was controlled by a gravimetric determination of the cobalt and sodium as sulfates. The  $i$  values indicate that the salt is tetra-ionic.

TABLE XI.

Concentration.		F.-P. depression, $\Delta t$ .	$\Delta t/N$ .	$i$ .
$N \times 10^3$ .	Equivalents (10) <sup>3</sup> .			
16.3	48.9	0.1098	6.74	3.63
31.2	93.5	0.2146	6.89	3.71

The values of the apparent ionizations of the cobaltammines, as determined by the conductivity and freezing-point methods, are nearly the same, with one exception, and that is in the case of the salt of highest type, hexammine cobaltic chloride, a tetra-ionic salt, which gives a value for the freezing-point lowering 1.2% higher at 0.005  $N$ , and 6.7% higher at 0.050  $N$ . These deviations are in the same direction as those found in this laboratory between the two sets of results for lanthanum nitrate, a salt of the same type. These are given in Table XII

TABLE XII.—VALUES OF THE APPARENT IONIZATION OF LANTHANUM NITRATE AS CALCULATED FROM FREEZING-POINT AND CONDUCTIVITY DATA.

Concn. in equivalents.	Apparent ionization.		Per cent. deviation.
	Conductivity.	Freezing point.	
0.005	85.83	88.9	3.58
0.01	81.77	85.4	4.44
0.05	69.91	75.4	7.86
0.1	64.38	71.6	11.21
0.2	58.51	68.8	14.46

With both of these tri-univalent salts the value of the apparent ionization calculated from the freezing-point results rapidly increases above that determined by conductivity as the concentration of the solution increases. This suggests that the cause of this change is to be sought in some factor which rapidly increases in value with the concentration of the solution. This result is very different from that which is found in the case of salts of simpler types, so even after making allowance for the fact that the freezing-point result depends upon the activity of the constituents of the salt, and the conductivity upon the number and speed of the ions, it still seems as though a large part of the deviation remains to be explained. It is interesting that this deviation is in the direction which would be predicted from the intermediate ion hypothesis as advanced by Harkins.<sup>1</sup>

#### Conductivity Measurements (by W. A. ROBERTS).

None of the salts whose conductivity was measured showed appreciable decomposition at 0° with the exception of trinitrotri-amine. At 25°

<sup>1</sup> See the fourth paper in this number of THIS JOURNAL.

all with the exception of the hexammine showed some change, but not enough to be considered in the time taken for measurement.

The cells used were the type devised by Kraus and used by Noyes, Melcher, Washburn and others. The cell used for the more concentrated solutions had a constant of 4.745 at  $0^\circ$ , and the one used for the more dilute solutions had a constant of 0.09710 at  $0^\circ$ . The conductivity of  $N/50$  KCl was taken as  $1.521 \times 10^{-3}$ .

For the calculation of the equivalent conductivities the hexammine was considered to have four, the pentammines three, and the tetrammines two ions, as determined by the freezing-point measurements. The value of  $\Lambda_0$  was found by plotting  $1/\Lambda$  against  $(CA)^{n-1}$ . The range of  $(n-1)$  was found to be from 0.4 to 0.8.

Measurements were begun upon sodium cobalt nitrite, but such rapid decomposition took place that the data were not recorded. Trinitro-triammine which is supposed by Werner not to be ionized showed the following molecular conductivities which are only about 1/20,000 that of the di-ionic croceo and flavo salts:

Molar concentration.....	0.000328	0.000737
Molar conductivity.....	0.004	0.003

TABLE I.—VALUES OF  $\Lambda$  AT  $0^\circ$  AND  $25^\circ$  WITH THE CORRESPONDING DENSITIES OF THE SOLUTIONS AT  $25^\circ$ .

C.	$\Lambda$ $25^\circ$ .	$\Lambda$ $0^\circ$ .	Densities $25^\circ/4^\circ$ .
	Hexammine Cobalt Chloride.		
0.1107	101.3	56.09	1.0022
0.07722	109.2	58.90	1.0003
0.05293	117.2	63.27	0.99955
0.02015	130.2	69.8	0.99775
0.002032	160.0	85.7	0.99720
0.0004315	172.0	91.0	.....
	Nitrotetrammine Cobalt Nitrate.		
0.01014	94.56	51.69	0.99870
0.004724	97.22	53.54	0.9977
0.002493	99.81	54.53	0.9974
0.0009658	101.9	55.71	0.9972
0.0004720	102.5	56.04	.....
	Nitrotetrammine Cobalt Chloride.		
0.009693	100.8	53.8	0.99810
0.004710	103.8	55.3	0.9976
0.002389	105.6	56.4	0.99730
0.001107	106.8	57.0	.....
0.0005205	108.9	57.8	0.9972
0.0001100	110.0	58.3	.....
	Chloropentammine Cobalt Chloride.		
0.0178	120.7	65.00	0.99821
0.008384	130.2	69.15	0.99760
0.003728	136.8	72.8	0.99729
0.0008891	142.8	75.25	0.99710
0.0003021	144.7	77.0	.....



TABLE I (continued).

C.	$\Lambda$ 25°.	$\Lambda$ 0°.	Densities 25°/4°.
Nitropentammine Cobalt Chloride.			
0.02061	116.0	62.25	0.9984
0.009910	122.4	.....	0.9977
0.004612	129.6	68.60	0.9973
0.001801	134.3	71.0	0.9972
0.001078	135.7	72.25	.....
0.0005492	137.5	72.70	.....

TABLE II.—APPARENT IONIZATION OF HEXAMMINE CHLORIDE AND LANTHANUM NITRATE.

Concentration.	$\Lambda/\Lambda_0$ .	$\sqrt[3]{\text{Concentration.}}$
Hexammine Cobaltic Chloride, $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ .		
0.05	63.8	0.3684
0.02	72.0	0.2714
0.01	76.9	0.2154
0.005	81.0	0.1709
0.002	85.8	0.1260
0.001	88.8	0.0794
0.0005	91.4	.....
Lanthanum Nitrate.		
0.2	58.5	.....
0.1	64.4	.....
0.05	69.9	.....
0.01	81.8	.....
0.005	85.8	.....
0.002	90.3	.....

**Magnesium Sulfate.**—The material used was "Zur Analyse" salt, which was recrystallized twice from conductivity water. The original solution was made up and analyzed. The other solutions were dilutions made at 25°.

TABLE III.—THE VALUES OF  $\Lambda$  AND  $\Lambda/\Lambda_0$  AT 18° AND 25° FOR  $\text{MgSO}_4$  AND THE DENSITIES OF THE SOLUTIONS AT 25°.

Equiv concn.	$\Lambda$ 25°.	$\Lambda/\Lambda_0$ 25°.	$\Lambda$ 18°.	$\Lambda/\Lambda_0$ 18°.	Densities 25°/4°.
0.0	135.0	.....	114.4	91.3	.....
0.00050635	123.3	91.33	104.4	87.4	.....
0.001067	117.4	86.96	100.1	82.7	.....
0.0020134	110.8	82.07	94.67	73.7	0.9972
0.0050635	99.0	73.33	84.35	66.5	0.9974
0.010067	88.85	65.82	76.15	58.7	0.99765
0.020134	78.98	58.50	67.23	49.3	0.9983
0.050635	66.05	48.90	56.54	43.3	1.000
0.10067	57.79	42.81	49.58	37.6	1.0033
0.20135	49.82	36.90	43.12	30.8	1.0092
0.50635	40.72	30.16	35.25	25.2	1.0269
1.0067	33.37	24.72	28.81	.....	1.0559

**Summary.**—The freezing-point lowerings of nine cobaltammines of different types have been determined. These salts, with the exception

of sodium cobaltic nitrite, were prepared by methods proposed by Jørgensen. On the whole, the results obtained from the freezing-point measurements, correspond very closely with those given by simple salts of like ionic types. Our results show that the type of each salt is the same as that assumed by Werner and his co-workers, but on the other hand they do not agree well with Werner's own freezing-point measurements. No explanation can be offered for the erroneous results given by Petersen's work, other than that his thermometric measurements must have been approximately 100% in error, except in the work on triamminotritinitro cobalt.

Conductance measurements have also been made on the same series of cobaltamines.

In conclusion, we wish to thank L. H. Adams and John Johnston of the Geophysical Laboratory in Washington, for the loan of the freezing-point apparatus and the interferometer, and to express our indebtedness for a grant of two hundred dollars from the Wolcott Gibbs Fund of the National Academy of Sciences.

CHICAGO, ILL.

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[CONTRIBUTIONS FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

## THE FREE ENERGY OF DILUTION AND THE FREEZING-POINT LOWERINGS IN SOLUTIONS OF SOME SALTS OF VARIOUS TYPES OF IONIZATION, AND OF SALT MIXTURES.

BY RALPH E. HALL AND WILLIAM D. HARKINS.<sup>1</sup>

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### I. Experimental.

The experimental work outlined in this paper was begun for the purpose of obtaining accurate freezing-point data from which the free energy of dilutions of dilute salt solutions can be determined. It seemed particularly desirable that accurate measurements should be carried out on higher type salts, in order that the results for salts of different types might be compared. It was found, too, that, while it is well known how mixtures of common ion salts in aqueous solution behave with respect to the conductivity of the separate salts, there are no similar data for the freezing-point lowerings of mixtures. This paper gives data for the freezing-point lowerings of uni-univalent, uni-bivalent, uni-trivalent, and bi-bivalent salts, and for mixtures containing two uni-univalent salts.

<sup>1</sup> This paper forms the basis for a part of a dissertation presented to the University of Chicago by Ralph E. Hall in part fulfilment of the requirements for the degree of Doctor of Philosophy.

The work of Adams<sup>1</sup> on freezing-point lowerings has given a simple method for investigations of this type, even in quite dilute solutions, and one which in general is probably the most accurate. The introduction of vacuum jars for containing the equilibrium mixture and the ice-water reference zero, in place of the beakers or platinum vessels used by previous investigators in this field, the use of a differential temperature measuring device, and the application of the Zeiss interferometer to the analysis of the equilibrium solutions, have made the attainment of accuracy in measurements at comparatively high dilutions a relatively simple matter. Adams' data cover only solutions of the nonelectrolyte mannite, and the salts potassium chloride and potassium nitrate. The present investigation extends the method, with slight changes, to salts of various types of ionization, and to equimolar mixtures of di-ionic salts, in which the known freezing-point data agree closely with those derived from conductivity measurements as regards the apparent degree of ionization.

#### The Apparatus.

**Thermoelement.**—A copper constantan element of fifty junctions was used.<sup>2</sup> In its construction, No. 36 copper wire, and No. 30 constantan wire, both double silk insulated, were used. The constantan wire was tested carefully for inhomogeneities<sup>3</sup> and any parts evidencing them were removed. The soldering of the couples, and the assembling of the element were done as recommended by Adams. The junctions, thoroughly insulated by waterproof varnish, and bound together in a small cone, were encased in glass tubing, and surrounded by naphthalene, the latter extending a little more than half the length of the tube. To insure against short circuits between the couples, and between the halves of the element, the resistance was tested frequently throughout the construction, and always at the beginning and close of a series of determinations. The wire, where exposed, and in the glass tube above the naphthalene, were treated with melted paraffin; a reinforcing brass rod was inserted, and this and the exposed wires were wrapped with silk ribbon. The latter was varnished to prevent as far as possible any chance for moisture to decrease the internal resistance. The thermoelement when not in use should be kept in a closed vessel containing  $P_2O_5$ .

The element was calibrated against a twenty-four junction element made by White, which had been standardized at the Bureau of Standards. Comparisons were made in a thoroughly stirred kerosene bath, and these

<sup>1</sup> THIS JOURNAL, 37, 481 (1915).

<sup>2</sup> This element was made at the Geophysical Laboratory in Washington. We wish to make acknowledgment of the courtesy of Dr. Day in granting permission for this; and of the coöperation of Drs. Adams, White and Johnston in its construction. We are also indebted to them for the loan of their freezing-point apparatus and interferometer.

<sup>3</sup> W. P. White, THIS JOURNAL, 36, 2296 (1914); L. H. Adams, *Loc. cit.*, footnote.

readings used in determining the relation of microvolts to temperature for the element. The solution of the cubic equation  $E = At + Bt^2 + Ct^3$  gave

$$E = 1879.7t + 2.52t^2 - 0.0057t^3.$$

The following data show how closely observed and calculated readings agree:

TABLE I.—DATA TAKEN FOR DETERMINING THE EQUATION OF THE THERMOELEMENT, AND FOR TESTING ITS ACCURACY.

$t^\circ$ determined by standard White couple.	$\mu v$ observed.	$\mu v$ calculated by equation.	Difference.
9.760	18580.8 <sup>1</sup>	.....	...
14.785	28326.8	28323.8	3.0
15.778	30263.0 <sup>1</sup>	.....	...
23.350	45194.0	45192.4	1.6
23.525	45539.7	45539.4	0.3
32.291	63134.8 <sup>1</sup>	.....	...
35.364	69366.0	69370.3	-4.3

It will be noted that the greatest deviation of observed from calculated values is a little less than one part in nine thousand. The differential of the above equation gives the gradient in microvolts per degree. For temperature differences of  $0.1^\circ$  or less, all terms but the first may be neglected, *i. e.*, microvolts may be converted into degrees by multiplying by 0.0005320. The second term, however, must be used for larger differences, but the third was entirely negligible for our freezing-point measurements, in which the greatest lowering was  $2.2^\circ$ .

The above equation for the thermoelement was based entirely on temperatures above  $0^\circ$ . To obtain a calibration below  $0^\circ$ , the freezing-point depressions of the alcohols mannite and erythrite were determined for a number of concentrations, and the deviations of the observed temperature from the theoretical at low concentration, calculated on the basis of  $1.858^\circ$  for the molal lowering of water, were accepted as the corrections necessary to apply. Reference to Table II will show that the above equation gave depressions consistently  $0.0001^\circ$  too small both with mannite and with erythrite, up to concentrations of  $0.0606 N$  for the former and  $0.0230 N$  for the latter. In the solutions of greater concentration than this, there is an increasing divergence between observed and calculated values, and in the other direction, *i. e.*, in the direction which corresponds to hydration. The analysis of the solutions of mannite by the interferometer was accurate to  $0.00001 N$ , and to  $0.00002 N$  for those of erythrite. A correction of  $0.0001^\circ$  has been made, accordingly, on all temperature readings for low concentrations, where this amount would affect the  $\Delta t/N$  values.

**Galvanometer.**—A Weston galvanometer, Model 89, was used. This

<sup>1</sup> Used in calculating the equation.

instrument gave a sensibility of 1 mm. on the scale per microvolt at approximately a meter's distance, so that the estimation of  $0.1 \mu v$  was entirely certain.

**Potentiometer.**—A double combination potentiometer (the first of this type to be constructed), recommended by White,<sup>1</sup> and constructed by the Leeds & Northrup Company, was used. One of the great advantages of this instrument is that by means of compensating coils, the resistance in the galvanometer circuit, and consequently the sensibility of the galvanometer, is maintained constant, whatever the potentiometer reading. A false top of glass, blackened on one side, raised about an inch above the top of the potentiometer has served to protect the hard rubber from the effects of light, and to shield the connections from any sudden changes of temperature. The switches were made from double throw copper knife switches of the pattern suggested by White. They were removed from their fiber bases, and set on a single sheet of hard rubber which was protected from the action of light at all times except when the system was in use. All soldered connections were made thermally neutral according to the method suggested by Wenner. The Weston standard cell was calibrated by the Bureau of Standards, and its factor given as 1.018348. Constancy of temperature was assured by placing it in an asbestos-lined chamber. The whole system, including the freezing-point apparatus, was doubly shielded as recommended by White,<sup>2</sup> and practically no trouble has been experienced from leakage currents at any time. An eliminating switch took care of any chance thermal electromotive forces, or other parasitic effects.

Fig. 1 is a diagram of the potentiometer and switchboard, with the accompanying batteries, standard cell, galvanometer, and rheostats. The dials designated by P correspond to one potentiometer, those marked P' to the other. The switches have the following significance: A is a key in the cadmium cell circuit, and F the same in the galvanometer circuit. BB', CC', DD', connect to various thermoelements; BB', when making the connections of B', has been closed by a resistance of 230 ohms, as this was the resistance of our 50 junction element, and this connection facilitated checking the sensibility of the galvanometer. EE', when in the position E', connects into the system thermoelements BB' and CC', and potentiometer P'; in position E, connects in thermoelements DD' and potentiometer P. GG' is a key which permits very low electromotive forces to be read directly by the deflection of the galvanometer. In position G, the potentiometer is connected in; in position G', the potentiometer is cut out, and an equal resistance substituted for it. HH' and II' regulate the sensibility of the galvanometer; with the switches

<sup>1</sup> THIS JOURNAL, 36, 1874 (1914).

<sup>2</sup> *Loc. cit.*



thermocouples.  $KK'$ , in position  $K$ , connects the cadmium cell with the terminals of the 1018 ohm resistance in the potentiometer, which in conjunction with rheostat  $R$  regulates the current from storage battery  $BL$ ; in position  $K'$ , connects it with the terminals of the 10180 ohm resistance, which with rheostat  $R'$  regulates the current from battery  $B2$ .  $LL'$  is the eliminating switch. In position  $L'$ , the circuits are adjusted for regular determinations; in position  $L$ , the currents from the batteries no longer run through the dial resistances of the potentiometer, but only through the fixed resistances and that of their rheostats. Also, the thermoelement has been cut out, and a resistance equal to it (230 ohms in this case) has been substituted in its place. The galvanometer setting on zero is made with the switch in this position; and as the switch was thoroughly tested for thermoneutrality, this setting will cut out practically all parasitic  $E. M. Fs.$  in the potentiometer, galvanometer, and switch-board from the reading of the thermoelement, when the switch is in position  $L'$ .

#### Freezing-Point Apparatus.—

This was the same apparatus used by Adams,<sup>1</sup> and needs no further description.

#### Experimental Procedure.

The apparatus was set up as shown in Fig. 2, with the exception that ice filled the upper portions of the stirring compartments in the vacuum jars. In the earlier work, the regular artificial ice was used. It was broken on an iron grating with a wooden pestle, and suitable sized pieces were chosen from the top of the grating and washed thoroughly with pure water before being placed in the vacuum jars. This ice when melted and compared with pure water seldom gave a reading of more than 3 divisions on the interferometer, and usually less, although on one occasion a reading of 11 divisions was noted.

The results of this series of

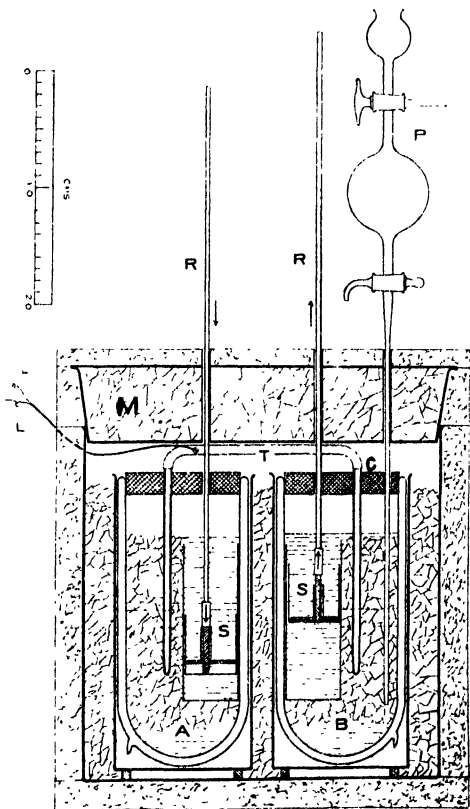


Fig. 2.—Cross-section of freezing-point apparatus.—Courtesy of L. H. Adams.

<sup>1</sup> *Loc. cit.*

freezing-point determinations were discarded, except for the more concentrated solutions, where the error involved became negligible. It was thought best, finally, to make ice from the laboratory distilled water, and thus avoid any chance of error from this source. A covered nickel-plated copper vessel,  $2 \times 20$  inches at the bottom,  $3 \times 20$  inches at the top, and 16 inches high, filled with water and placed in an ice salt mixture, froze solid overnight, and gave ample ice for both freezing-point jars. To the ice and water in pan M, Fig. 2, a little salt was added, and the temperature in the air space above the vacuum jars was noted by means of a single couple introduced at C. The apparatus was allowed to stand for a few hours, during which the vessels were stirred occasionally, and the zero reading of the potentiometer observed. Usually this would change very slowly for the first hour, but would then remain constant for an indefinite period. This reading varied from  $1.0 \mu v$  to  $2.0 \mu v$  during the year it was under observation, and as Adams suggests, probably represented not a difference in temperature ( $0.0005$ – $0.001^\circ$ ) between the two vessels, but a summation of several small electromotive forces in the system apart from those excluded by the eliminating switch. Hausrath<sup>1</sup> and Flügel<sup>2</sup> have noted this same zero reading in their freezing-point work. That it can have no detrimental effects on the differential temperature determinations is evidenced by its constancy, when equilibrium is finally attained, and by the data obtained on the nonelectrolytes erythrite and mannite.

By the time the apparatus was in equilibrium, the air chamber above the freezing-point vessels had assumed a temperature which varied in the different determinations between  $-0.2^\circ$  and  $-0.3^\circ$ , but which was usually more nearly  $0^\circ$  than this. At the close of a series, some 3 or 4 hours later, this temperature had risen to about  $0.5^\circ$  or  $0.6^\circ$ . It is to be noted that this convergence temperature, in view of the large amount of ice in the equilibrium mixture, could have no appreciable effect. The convergence temperatures noted during the work on erythrite and mannite are included in Table II.

The final procedure was as follows: When equilibrium was definitely attained, the zero reading of the potentiometer thermoelement system was taken, and a sample of water (the zero sample for the interferometer) was withdrawn through the pipet, and an equal amount of chilled water containing the desired amount of salt was introduced. The solution was then stirred until equilibrium was reached, when the pipet was rinsed by partially filling it with the freezing mixture, and giving it a rotary motion. When this liquid had flowed back into the freezing-point vessel, stirring was resumed until the temperature had become stationary again.

<sup>1</sup> *Drude's Ann.*, **9**, 522 (1902).

<sup>2</sup> *Z. physik. Chem.*, **79**, 579 (1912).



In order that the heat developed by the stirrers should have no effect, and to make certain that the true equilibrium point had been reached, the apparatus was allowed to stand for a few minutes without stirring, the reading of the potentiometer was noted, and then the solution was again agitated. The apparatus was allowed to stand a second time for several minutes, during which the temperature was noted. If the equilibrium temperature proved to be the same as before, this was taken as the correct value, and a sample of the solution was removed through the pipet; if not, the process was repeated until the second reading was in accord with the one preceding. With the dilute solutions, the equilibrium temperature once attained would show no change for a half hour or more, and in the more concentrated solutions, the change was slight over a like period. After removal of the sample for analysis, a second quantity of salt was introduced as before, and the same procedure followed until the desired number of points had been taken.

**Effect of Air on the Freezing-Point Lowering.**—The determinations were made in such a way as to eliminate the very considerable error which may be caused by the presence of dissolved air on the freezing-point lowering. In both of the Dewar flasks the ice and the water used were from the same samples, and the contents of both were stirred to the same extent for several hours preceding the run, until no change in the reading during an hour or more could be detected. Also, blank runs were made, under the same conditions. It was found, using these precautions, that no difference in temperature ( $\Delta t$ ) between the contents of the two Dewar flasks, could be detected, which in any case resulted from the solutions of unequal amounts of air in the two liquids.

**Analysis of the Equilibrium Solution.**—The concentration of the samples taken from the equilibrium mixture was determined by the Zeiss interferometer,<sup>1</sup> except in the case of the iodates. In the determinations on potassium sulfate, barium chloride and magnesium sulfate, the second method outlined by Adams was followed. The zero point of the interferometer was determined by placing distilled water in both chambers, and noting the scale reading. Then the sample of water from the freezing-point apparatus (the zero sample mentioned above) was substituted in one chamber. Usually a reading of one or two divisions was noted, and this was the real zero for the series of unknown salt solutions to be determined. With ice made from the laboratory distilled water, the zero reading was not more than one-half scale division. Solutions of nearly the same strength as the unknown, one a little more, the other a little less concentrated, were next placed in the chambers of the interferometer and the scale reading noted. From the difference between this and the original zero, and between the solutions, a linear gradient over a small

<sup>1</sup> Discussed by Adams, *THIS JOURNAL*, 37, 1181 (1915).

range of concentration can be obtained. Finally, the unknown was substituted for one of the known solutions, and the scale reading noted, whence the concentration could be determined at once. For the other salts analyzed by the interferometer, a slightly different method was used. One or two determinations of the gradient were made. Then a solution was prepared similar in concentration to the unknown, and a comparison made, from which the concentration of the unknown could be almost exactly calculated. Finally, a solution was made of almost exactly this concentration, and compared with the unknown. At low concentrations, this solution would differ from the unknown by no more than 1-10 divisions of the interferometer, and in the quite concentrated solutions by only 50-100 divisions, thus obviating any possibility of mistaking the band to be read, and any error due to interpolation by the gradient. These methods both presume a knowledge of the approximate concentration of the unknown solutions. Usually this is the case; but if not, a comparison of the most dilute solution with water will give its strength, and from this, an approximation of the other solution strengths can be made.

If we assume an accuracy in setting equal to one scale division, the interferometer will be correct to 0.0002% in the case of most salts.<sup>1</sup> An error of this amount, however, with dilute solutions of cobalt chloride (0.0035 *N*) represents an error of 1% figured on the basis of total salts and similarly with all salts of small equivalent weight. For the determination of the unknown solutions of the iodates, therefore, titrations were made with thiosulfate.

**Calculation of Data.**—All weights taken were corrected to values *in vacuo*, and all solutions were calculated on the basis of weight normality. In calculating the values of *i*, the equation  $iN = \Delta t(1 + 0.0055 \Delta t)/1.858$  was used.<sup>2</sup> For the apparent degree of ionization, the values were obtained by the usual equation  $i = 1 + (n - 1)\gamma$ . *N* refers to the number of mols of solute to 1000 g. of water, *n* to the number of ions into which the salt dissociates, and  $\gamma$  to the apparent degree of ionization.

#### Experimental Data.

**Mannite and Erythrite.**—Kahlbaum's pure materials were used. The mannite was twice recrystallized from pure water. The melting point of the air-dry crystals, as determined by Hedenburg, was 167.3°. It was finally dried at 100° for a few hours, and then at 120° for 4 hours. The erythrite was twice recrystallized from a weak alcohol solution; final drying was at 115° for a few hours.

The freezing-point lowerings of these nonelectrolytes was determined primarily to test the accuracy of the potentiometer system and the thermo-

<sup>1</sup> L. H. Adams, *THIS JOURNAL*, 37, 1187 (1915).

<sup>2</sup> *Ibid.*, 32, 1011 (1910).

element equation. At the low concentrations, the deviation between observed and theoretical values is consistently approximately  $0.0001^\circ$ , the greatest deviation being  $0.00014^\circ$  in erythrite at a concentration  $0.00483$  formal. This correction was consequently applied to all measurements at low concentration. The  $0.0628$  formal solution of erythrite, and the  $0.1197$  formal solution of mannite, however, show considerable deviation from the theoretical values, as calculated by the equation given above, and the magnitude of this increases with increase in concentration. The deviation is in the same direction as with cane sugar,<sup>1</sup> in which Washburn<sup>2</sup> has shown rather definitely that this departure from the theoretical is due to hydration, and also the same as with levulose<sup>3</sup> and dextrose.<sup>4</sup> In Fig. 3 the cube root of the temperature lowering has been plotted against the cube root of the mol fraction. With the exception of the last point on erythrite, no deviation from a straight line can be noted,

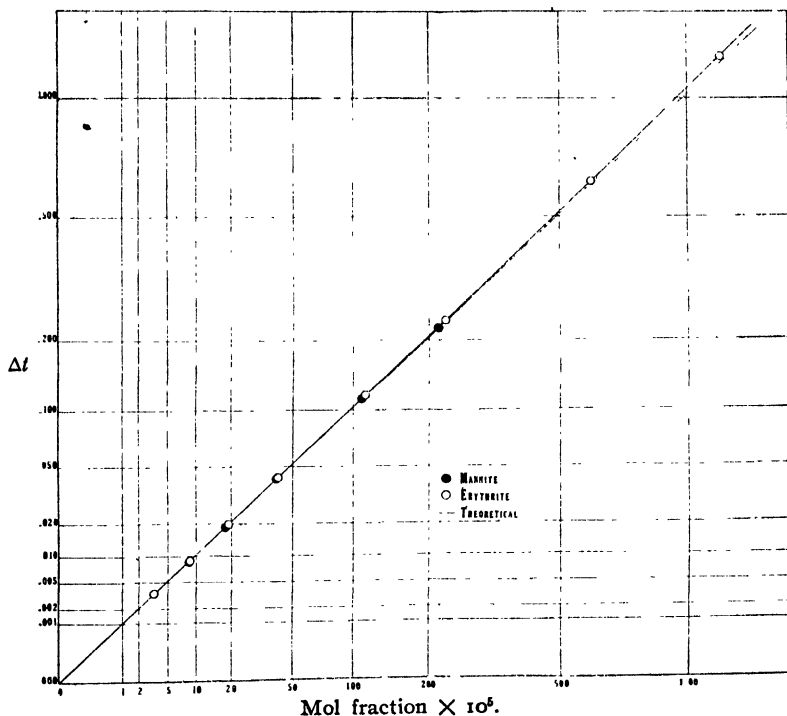


Fig. 3.

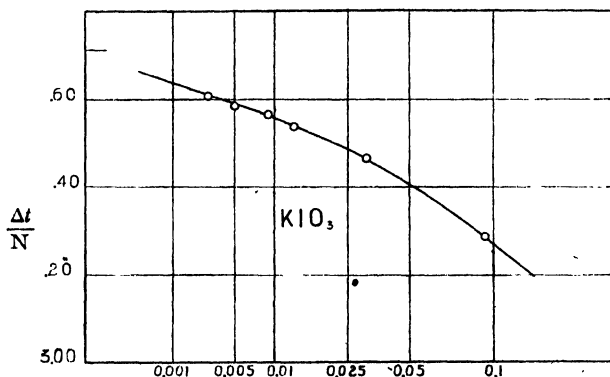
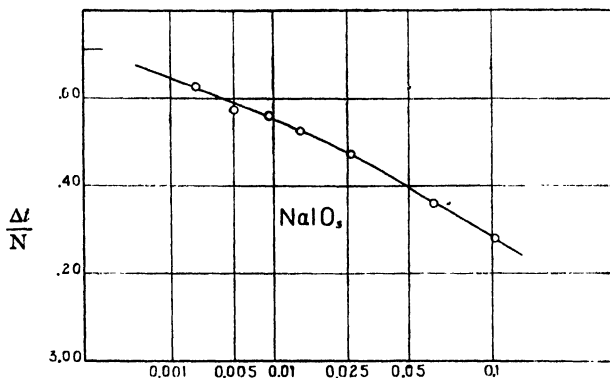
<sup>1</sup> Loomis, *Z. physik. Chem.*, **32**, 591 (1900); Ewan, *Ibid.*, **31**, 27 (1899); Morse and Frazer, *Am. Chem. J.*, **34**, 1 (1905).

<sup>2</sup> *Technology Quarterly*, **21**, 376 (1908); also "Principles of Physical Chemistry,"

<sup>174</sup>.

<sup>3</sup> Jones, "Hydrates in Aqueous Solution," *Carnegie Inst. Pub. No. 60* (1907).

<sup>4</sup> Roth, *Z. physik. Chem.*, **43**, 560 (1903); Jones, *Loc. cit.*



Equivalent concentration (cube root plot).

Fig. 4.

although the curve shows an appreciable deviation from the theoretical at the higher concentrations. The values given by Jones<sup>1</sup> and Loomis<sup>1</sup> on mannite in concentrated solutions show a large deviation from the theoretical curve.

Table II contains the complete data on erythrite and mannite, and shows the deviation of the observed temperature depression from the theoretical, assuming the concentration as correct, and the difference in concentration from the theoretical, assuming the temperature measurement as correct.

TABLE II.—FREEZING-POINT DATA ON ERYTHRITE AND MANNITE.

Conc. $N \times 10^3$	F.-P. depression.		Diff. $\times 10^4$	$N \times 10^3$ (calc.).	Diff. millimols.	Temp. in equilibrium chamber.
	$t^\circ$ (obs.).	$t^\circ$ (calc.).				
Erythrite.						
1.85	0.00338	0.00343	0.5	1.82	0.03	-0.02
4.83	0.00883	0.00897	1.4	4.75	0.08	+0.04
10.57	0.01958	0.01964	0.6	10.55	0.02	0.10
23.00	0.04273	0.04271	0.1	22.99	0.01	0.13
62.84	0.11710	0.11663	4.7	63.09	0.25	0.18
127.14	0.2375	0.2357	18	128.1	1.0	0.26
335.5	0.6304	0.6196	108	341.3	5.8	0.26
652.4	1.2371	1.1981	390	673.7	21.3	0.31
Mannite.						
4.72	0.00867	0.00877	1.0	4.67	0.05	-0.16
10.06	0.01846	0.01859	1.3	9.94	0.12	0.12
22.49	0.04171	0.04178	0.7	22.45	0.04	0.10
60.62	0.11265	0.11257	0.9	60.67	0.05	0.10
119.7	0.2225	0.2221	4.0	119.9	0.2	0.10

<sup>1</sup> Loc. cit.

**Sodium and Potassium Iodates.**—The pure salts were twice recrystallized (the sodium salt but once) from distilled water. The potassium iodate was dried by heating at  $160^\circ$  for several hours, the sodium salt by like heating at  $150^\circ$ . These salts were chosen, as the work of Jahn<sup>1</sup> had shown that their freezing-point lowerings were practically identical at all concentrations he investigated, and the data collected by Noyes and Falk<sup>2</sup> showed that the apparent degree of ionization as determined by the freezing-point method coincided very closely with that obtained by conductivity measurements. They also show that within the limit of experimental error no difference from the temperature depressions given by the pure salts can be detected in the freezing-point lowerings of the equimolar mixture. Fig. 4 shows the values of  $\Delta t/N$  plotted against the cube root of the concentration; Fig. 5 brings together on the same curve the values for the pure salts, and for the equimolar mixture.

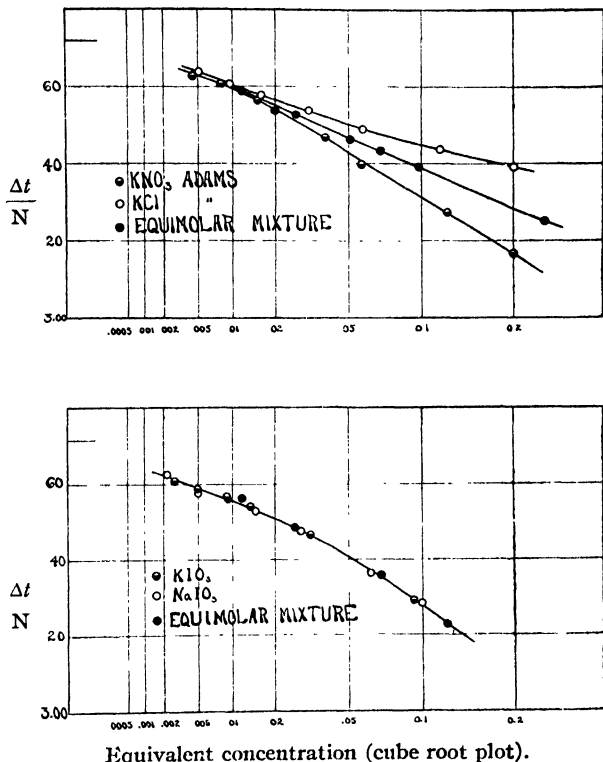


Fig. 5.

Table III contains the complete data, and Table IV the  $\Delta t/N$  values at rounded concentrations, the value of  $i$ , and the corresponding degree of dissociation. Jahn's values for  $i$  are included for comparison.

Table III contains the complete data, and Table IV the  $\Delta t/N$  values at rounded concentrations, the value of  $i$ , and the corresponding degree of dissociation. Jahn's values for  $i$  are included for comparison.

**Equimolar Mixture of Potassium Chloride and Potassium Nitrate.**—Pure commercial salts were twice recrystallized from pure water, and dried for several hours at  $160^\circ$ .

Only the equimolar mixture was used, as Adams had determined the values for the pure salts with the same apparatus. Table V contains the

<sup>1</sup> *Z. physik. Chem.*, **59**, 37 (1907).

<sup>2</sup> *THIS JOURNAL*, **34**, 454 (1912).

TABLE III.—FREEZING-POINT DATA ON POTASSIUM IODATE, SODIUM IODATE AND THEIR EQUIMOLAR MIXTURES.

Conc. N X 10 <sup>3</sup> .	F.-P. depres- sion, $\Delta t$ .	$\Delta t/N$
Potassium Iodate.		
2.74	0.00990	3.609
5.06	0.01815	3.587
9.03	0.03220	3.568
13.58	0.04810	3.541
32.44	0.1125	3.466
93.80	0.3085	3.289
Sodium Iodate.		
2.12	0.00770	3.628
4.99	0.01785	3.576
9.29	0.00310	3.563
15.02	0.05300	3.529
28.68	0.0997	3.477
63.29	0.2129	3.363
101.0	0.3317	3.282
Equimolar Mixture.		
11.70	0.04170	3.563
26.75	0.0933	3.487
69.84	0.2350	3.357
123.9	0.4001	3.229

TABLE IV.—DATA ON POTASSIUM AND SODIUM IODATES, AND THEIR EQUI-MOLAR MIXTURES AT ROUNDED CON-CENTRATION.

Conc. N X 10 <sup>3</sup> .	$\Delta t/N$ .	$i$ .	$i$ (Jahn).	$\gamma$ .
Potassium Iodate.				
2	3.61	1.94	.....	94.0
5	3.584	1.929	1.941	92.9
10	3.560	1.916	1.913	91.6
20	3.512	1.890	1.882	89.0
50	3.406	1.835	1.828	83.5
100	3.271	1.764	1.765	76.4
Sodium Iodate.				
2	3.63	1.95	.....	95.0
5	3.595	1.934	1.939	93.4
10	3.560	1.915	1.916	91.5
20	3.510	1.890	1.890	89.0
50	3.401	1.832	1.842	83.2
100	3.287	1.772	1.773	77.2
Equimolar Mixture.				
10	3.565	1.918	1.912	....
20	3.515	1.892	1.890	....
50	3.408	1.835	1.834	....
100	3.277	1.767	1.768	..

original data, and Table VI that at rounded concentrations. The latter shows how closely the  $i$  values compare with the average of the  $i$  values for the pure salts at like concentrations. The last values for the pure salts were taken from the "best values" of Noyes and Falk,<sup>1</sup> as Adams' data extended only to 0.1 formal. Fig. 6 shows the relations of the curves.

**Magnesium Sulfate.**—A pure sample of salt was twice recrystallized from pure water.

The determination was made to extend the present method to this type of salt. The values obtained agree very closely with those of Loomis,<sup>2</sup> Hausrath,<sup>3</sup> and Bedford,<sup>4</sup> but as might be expected from the method of supercooling employed by him, are considerably different from those of Jones.<sup>5</sup>

Fig. 7 shows the curve, and Tables VII and VIII contain the data. Bedford's data are included for the rounded concentrations.

<sup>1</sup> THIS JOURNAL, 32, 1020 (1910).

<sup>2</sup> Wied. Ann., 51, 500 (1894).

<sup>3</sup> Ann. Phys., [4] 9, 522 (1902).

<sup>4</sup> Proc. Roy. Soc., 83A, 454 (1910).

<sup>5</sup> Z. physik. Chem., 11, 541 (1893).

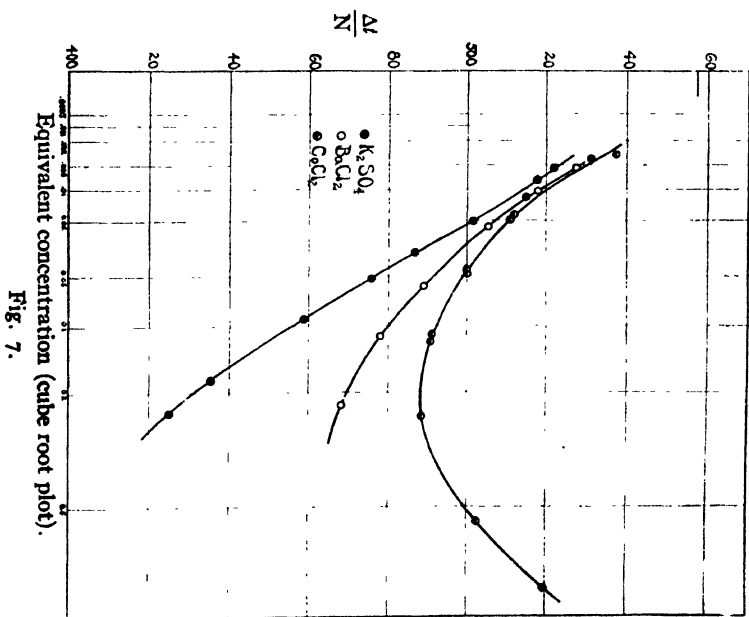
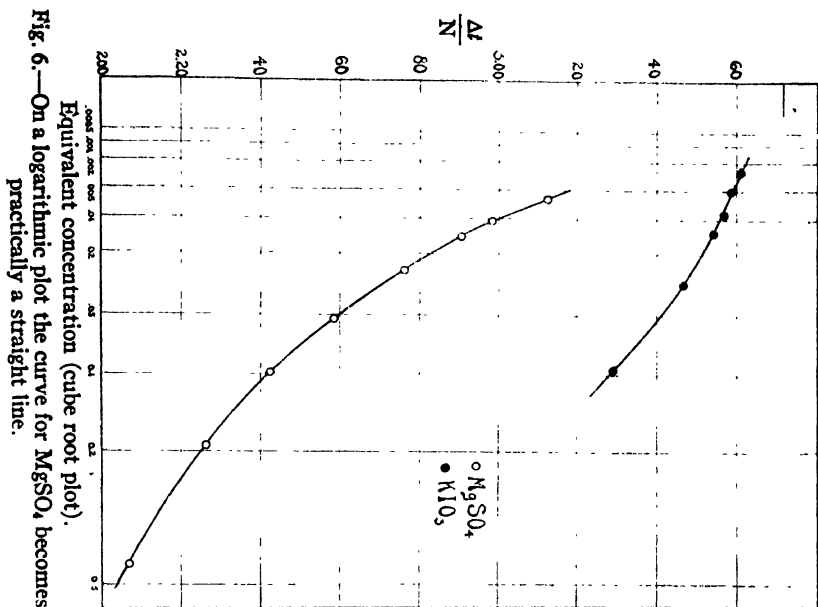


TABLE V.—DATA TAKEN ON EQUIMOLAR MIXTURES OF POTASSIUM CHLORIDE AND POTASSIUM NITRATE.

Conc. $N \times 10^3$ .	F.-P. depression, $\Delta t$ .	$\Delta t/N$ .
11.84	0.0425 <sub>0</sub>	3.590
19.98	0.0707 <sub>0</sub>	3.538
26.35	0.0929	3.529
50.91	0.1763	3.462
70.03	0.2405	3.434
98.63	0.3344	3.390
243.95	0.7927	3.250

TABLE VI.—DATA AT ROUNDED CONCENTRATIONS FOR THE POTASSIUM CHLORIDE-POTASSIUM NITRATE MIXTURE.

Conc. $N \times 10^3$ .	$\Delta t/N$ .	$i$ .	$i$ (av.) (Adams).
10	3.60	1.94	1.94
20	3.555	1.914	1.915
50	3.468	1.868	1.868
100	3.390	1.827	1.824
200	3.283	1.773	1.772

TABLE VII.—DATA ON MAGNESIUM SULFATE.  
Concentration.

$N \times 10^3$ .	Equivalents (10) <sup>3</sup> .	F.-P. depression, $\Delta t$ .	$\Delta t/N$ .
3.201	6.40	0.0100 <sub>0</sub>	3.124
5.35	10.71	0.0159 <sub>6</sub>	2.981
7.46	14.92	0.0216 <sub>8</sub>	2.902
13.10	26.21	0.0361 <sub>8</sub>	2.760
26.68	53.35	0.0673 <sub>0</sub>	2.582
48.78	97.56	0.1182	2.423
95.66	191.31	0.2163	2.261
221.0	442.1	0.4566	2.066

TABLE VIII.—MAGNESIUM SULFATE-ROUNDED CONCENTRATIONS.

Concn. equiv. (10) <sup>3</sup> .	$\Delta t/N$ .	$i$ .	$i$ (Bedford).	$\Delta t/N$ .
5	3.175	1.708	1.700	70.8
10	3.000	1.614	1.599	61.4
20	2.825	1.520	1.506	52.0
50	2.589	1.394	1.396 (Loomis)	39.4
100	2.420	1.303	1.283	30.3
200	2.252	1.214	1.205	21.4
300	2.156	1.162	1.154	16.2
400	2.090	1.128	1.117	12.8
500	2.036	1.099	1.084	9.9

**Potassium Sulfate, Barium and Cobalt Chlorides.**—The potassium sulfate and barium chloride were twice recrystallized from pure water. The cobalt chloride was made by dissolving the carbonate in hydrochloric acid, filtering off the excess carbonate, and crystallizing after the addition of three or four drops of hydrochloric. The crystals obtained were dissolved and recrystallized from the solution to which no acid had been added. The stronger solutions gave a slight acid reaction to litmus.

The determination with cobalt chloride was made to obtain data for comparison with the freezing-point results on the cobaltammines, since no data were available on dilute solutions of this salt. The values of Biltz,<sup>1</sup> and of Jones and Getman,<sup>2</sup> on the more concentrated solutions,

<sup>1</sup> *Z. physik. Chem.*, **40**, 200 (1902).<sup>2</sup> *Am. Chem. J.*, **31**, 322 (1904).



give curves similar in shape to ours, but differently placed, as may be seen by noting the values for  $\Delta t/N$  at rounded concentrations in Table X. The determinations on barium chloride and potassium sulfate were made with the intention to work on mixtures with these types of salts, but this has not been done as yet. The value of  $\Delta t/N$  for the most dilute concentration of barium chloride is higher than that obtained by Bedford<sup>1</sup> at this concentration, but on the whole our values agree very well with his. The  $i$  values for potassium sulfate and barium chloride at rounded concentrations are compared with those of Osaka<sup>2</sup> (with those of Archibald at points not reached by Osaka's data) and Bedford,<sup>3</sup> respectively; the latter were calculated from the rounded concentration  $\Delta t/N$  values summarized by Noyes and Falk.<sup>4</sup>

It is interesting to note the shape of the curves in Fig. 8 in the concentrated solutions. The cobalt chloride curve shows a departure from the ordinary form of curve in dilute solutions, the barium chloride is slower in showing the change, and potassium sulfate has just begun to show this effect in the most concentrated solutions taken. It will be noted, too, that the curve which shows this effect first, is the one which gives the highest values for  $\Delta t/N$  in dilute solutions, so that probably its influence extends even to the dilute solutions. The same thing

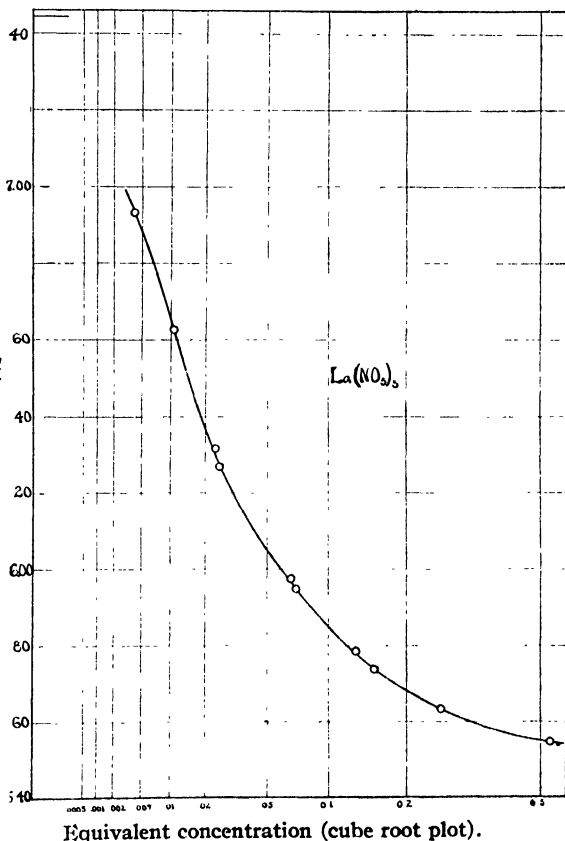


Fig. 8.

<sup>1</sup> *Loc. cit.*

<sup>2</sup> *Z. physik. Chem.*, 41, 560 (1902).

<sup>3</sup> *Trans. Nova Scotian Instit. of Science*, 10, 44.

<sup>4</sup> *THIS JOURNAL*, 32, 1011 (1910).

may be seen in the curve for lanthanum nitrate, and here, too, the break in the curve comes at a comparatively dilute point. It will be observed that this break comes sooner, the less basic the metallic element. Also, as pointed out by Jones, the substance with the largest amount of water of hydration gives the largest freezing-point depression, pointing to hydration in the solution.

Tables IX and X summarizes the data on these three salts, and Fig. 8 represents their curves plotted in the usual manner.

TABLE IX.—SUMMARY OF THE DATA TAKEN ON POTASSIUM SULFATE, BARIUM CHLORIDE AND COBALT CHLORIDE.

Concentration. N X 10 <sup>3</sup> .	Equiva- lents (10) <sup>3</sup> .	F.-P. de- pression, $\Delta t$ .	$\Delta t/N$ .
Potassium Sulfate.			
2.74	5.48	0.01430	5.219
4.04	8.07	0.0290	5.173
6.18	12.36	0.03180	5.147
10.39	20.78	0.05210	5.014
17.56	35.12	0.0855	4.866
26.08	52.15	0.1241	4.759
45.47	90.93	0.2085	4.586
88.99	177.97	0.3874	4.354
120.5	240.9	0.5120	4.250
Barium Chloride.			
2.73	5.45	0.01440	5.275
5.34	10.68	0.02760	5.178
11.42	22.83	0.0577	5.052
29.82	59.64	0.1458	4.889
56.11	112.22	0.2682	4.780
113.58	227.15	0.5319	4.683
Cobalt Chloride.			
1.73	3.46	0.00930	5.375
2.09	4.17	0.01110	5.311
8.92	17.84	0.04570	5.129
10.08	20.16	0.0515	5.108
22.51	45.02	0.1125	4.997
23.75	47.50	0.1188	5.003
54.75	109.50	0.2687	4.908
59.73	119.46	0.2930	4.906
125.6	251.2	0.6134	4.884
277.2	554.4	1.3934	5.026
421.7	843.4	2.1900	5.193

TABLE X.—SUMMARY OF DATA AT ROUNDED CONCENTRATIONS FOR POTASSIUM SULFATE, BARIUM CHLORIDE AND COBALT CHLORIDE.

Concn. equiva- lents (10) <sup>3</sup> .	$\Delta t/N$ .	$i$ .	$i$ (Osaka).	$\gamma$ .
Potassium Sulfate.				
5	5.258	2.830	2.846	91.5
10	5.150	2.772	2.787	88.6
20	5.020	2.701	2.704	85.1
		(Archibald)		
50	4.767	2.567	2.570	78.4
100	4.549	2.451	2.476	72.6
200	4.314	2.327	2.347	66.4
Barium Chloride.				
5	5.290	2.847	2.789	92.4
10	5.185	2.790	2.741	89.5
20	5.075	2.730	2.691	86.5
50	4.915	2.647	.....	82.4
100	4.796	2.585	.....	79.3
200	4.698	2.535	.....	76.8
Cobalt Chloride.				
5	5.311	2.858	$\Delta t/N$	..... 92.9
10	5.208	2.802	Biltz	Jones 90.1
20	5.107	2.749	.....	..... 87.5
50	4.989	2.687	5.05	..... 84.4
100	4.918	2.650	4.955	5.03 82.5
200	4.882	.....	4.905	4.95 ....
300	4.900	.....	4.930	4.93 ....
400	4.946	.....	4.990	4.935 ....
500	4.997	.....	5.05	5.00 ....

**Lanthanum Nitrate.**—We are indebted for our lanthanum nitrate to Dr. Miner of the Welsbach Co. This was in the form of its double ammonium salt. To obtain the pure substance, the lanthanum was precipitated as the oxalate, washed repeatedly until free from ammonia,

dried, and changed to the oxide by ignition. While the oxide was not pure white in color, spectroscopically it showed no evidence of impurities. We are indebted to Mr. Aronberg for this examination. The oxide was dissolved in strong nitric acid, in such amount that a small excess of oxide remained, and a clear solution was obtained by filtering. According to Noyes and Johnston,<sup>1</sup> this method of preparing lanthanum nitrate gives a neutral solution; but in the concentrated solutions which we made in this way, a slight acid reaction toward litmus was always noticeable. Finally, by evaporation *in vacuo*, the salt was obtained in the hydrated crystalline form.

The work on lanthanum nitrate was undertaken because we wished data on this type of salt for comparison with some of the cobaltammines. Noyes and Johnston determined the freezing-point lowerings in strong solutions, but no data were found for the dilute solutions.

Table XI contains the experimental data on this salt, and Table XII gives the values at rounded concentrations. It also gives for comparison the values of  $\Delta t/N$  obtained by Noyes and Johnston.

TABLE XI.—SUMMARY OF DATA TAKEN ON LANTHANUM NITRATE.

Concentration.		F.-P. depression, $\Delta t$ .	$\Delta t/N$ .
$N \times 10^3$ .	Equivalents (10) <sup>3</sup> .		
1.32	3.95	0.0091 <sub>8</sub>	6.931
3.54	10.61	0.0234 <sub>8</sub>	6.624
8.06	24.18	0.0509 <sub>0</sub>	6.315
8.57	25.72	0.0537	6.265
22.22	66.67	0.1328	5.973
23.60	70.80	0.1404	5.948
43.37	130.11	0.2508	5.782
51.19	153.57	0.2937	5.736
86.61	259.83	0.4878	5.631
174.86	524.58	0.9698	5.546

TABLE XII.—SUMMARY OF VALUES AT ROUNDED CONCENTRATIONS FOR LANTHANUM NITRATE.

Equivalents (10) <sup>3</sup> .	$\Delta t/N$ .	$\Delta t/N$ . (Johnson.)	$i$ .	$\gamma$ .
5	6.865	....	3.694	89.8
10	6.650	....	3.578	85.9
20	6.392	....	3.440	81.3
50	6.060	6.0	3.261	75.4
100	5.844	5.79	3.149	71.6
200	5.679	5.71	3.063	68.8
300	5.610	....	3.029	67.6
400	5.574	....	3.012	67.1
500	5.550	....	3.002	66.7

**Summary.**—A potentiometer system was installed, and a fifty-junction thermoelement constructed and standardized. The accuracy of temperature measurements of this system was checked by freezing-point determinations on the nonelectrolytes mannite and erythrite. In the dilute solutions, the greatest divergence in temperature from the theoretical was  $0.00014^\circ$ . As this deviation was consistently  $0.0001^\circ$ , it was used as a correction for the freezing-point depressions at low concentrations for all salts investigated. The accuracy of the system for greater differences of temperature was further checked by the readings in microvolts of a single couple, standardized at the Geophysical Laboratory against the vapor of boiling water, naphthalene and benzophenone. Our system was

<sup>1</sup> THIS JOURNAL, 31, 1008 (1909).

repeatedly tested with the water-vapor point, and found to agree in all cases well within the limit of error.

The freezing-point lowerings of various salts at different concentrations have been determined, their  $\Delta t/N$  values plotted against the cube root of the concentration, and their ionization values, as derived by this method, tabulated at rounded concentrations. Comparisons have been made with the values found in the literature; these have been chosen with the view of citing those obtained by the most accurate methods.

The freezing-point lowerings of two equimolar mixtures of di-ionic salts have been determined for concentrations between 0.01 and 0.1 or 0.2 formal; and over the range investigated, the values of  $i$  agree very closely with those obtained by averaging the  $i$  values for the pure salts at like concentrations.

In conclusion, we wish again to make acknowledgment of the courtesy of the staff at the Geophysical Laboratory for their coöperation; to acknowledge the advance of funds from the Wolcott Gibbs Fund of the National Academy for the installation of the potentiometer and galvanometer; and to thank the donors of the Swift Fellowship.

CHICAGO, ILL.

[CONTRIBUTION FROM KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

## THE FREEZING-POINT LOWERINGS IN AQUEOUS SOLUTIONS OF SALTS AND MIXTURES OF SALTS AND OF A SALT WITH A NONELECTROLYTE.

BY WILLIAM D. HARKINS AND W. A. ROBERTS.

Received September 1, 1916.

The apparatus and methods of analysis were the same as used by Harkins, Hall and Roberts, in the measurements of the freezing-point lowerings of the cobaltammines.

In the study of the effect of a nonelectrolyte on a salt, a mixture of mannite and KCl was used. The solutions were in the ratio of molar mannite to two molar KCl. The values of  $\Delta t$  for mannite in the table were calculated on the basis that a molar solution of mannite gives a depression of the freezing point of  $1.859^\circ$ . The data for  $\Delta t/N$  for KCl alone were taken from the work of Adams.<sup>1</sup>

TABLE I.—TEMPERATURE LOWERING AND VALUES OF  $\Delta t/N$  FOR THE KCl MANNITE MIXTURE.

Conc. mannite.	Conc. KCl.	Total $\Delta t$ .	$\Delta t$ mannite.	$\Delta t$ KCl alone.	KCl in $\Delta t/N$ for mixture.	$\Delta t/N$ for KCl. Adams.	Temperature deviation in degrees.
0.00493	0.00987	0.04479	0.00927	0.03557	3.599	3.604	0.00005
0.01071	0.02153	0.09676	0.02012	0.07670	3.560	3.562	0.00006
0.021	0.04367	0.1940	0.4061	0.15343	3.511	3.512	0.00004
0.04067	0.08134	0.3570	0.0757	0.2813	3.466	3.466	0.0000

<sup>1</sup> THIS JOURNAL, 37, 481 (1915).

Only one set of determinations of the effect of mixtures on the freezing-point lowering could be found in the literature.<sup>1</sup> In each of the four experiments recorded the values given for the mixtures were farther from the experimental value of the salt alone than the deviation here found, but this difference may be due to the choice of mannite and potassium chloride in this particular case.

Unless there are two opposing effects which happen to cancel each other these results seem to indicate that the osmotic pressure of neither the mannite nor the potassium chloride is affected by the presence of the other in the mixture. Therefore the great increase in activity which the nonionized part of a salt exhibits, provided the present methods for the calculation of the ionization of salts is anywhere nearly correct, could not be attributed to the effect of the ions upon the activity of the nonionized part of the salt, if the nonionized part of a salt acts at all in a similar way to mannite. In other words, it seems necessary to conclude that either our present methods for the calculation of ionization are incorrect or else the nonionized part of a salt is very different in its make-up from a substance such as sugar. Assuming our present ionization values as correct there seems to be evidence to show that the un-ionized part of a salt is joined together extremely loosely. However, even on this basis it is very difficult to account for the extremely great increase in activity found for the nonionized part of the salt. Thus the solubility of the ionized part of thallos chloride is decreased from 17.55 to 9.7 millimols by the presence of 0.1 normal potassium nitrate solution, a decrease of 44.7% which represents an enormous increase in the activity of the nonionized salt.

Bates obtains somewhat similar results by calculations of freezing-point and conductivity data, and shows that at 0.1 normal the osmotic pressure of the "undissociated molecules" is 1.35 times greater than corresponds to van't Hoff's law.

TABLE II.—FREEZING-POINT LOWERINGS IN A 1 : 1  $\text{Na}_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4$  MIXTURE AND IN SOLUTIONS OF THE SALTS SEPARATELY.

Sodium sulfate.		Potassium sulfate.		Equimolar mixture of sodium and potassium sulfate.	
$\Delta t/N$ .	Equivalent concentrations	$\Delta t/N$ .	Equivalent concentrations.	$\Delta t/N$ .	Equivalent concentrations.
5.089	0.004733	5.219	0.005482	5.155	0.006781 <sup>1</sup>
4.945	0.01035	5.173	0.008071	4.972	0.01844
4.806	0.02222	5.147	0.01236	4.792	0.04305
4.585	0.04946	5.014	0.02078	4.610	0.08715
4.348	0.1004	4.866	0.03512	4.300	0.2065
4.064	0.1996	4.759	0.05215	3.939	0.5054
		4.586	0.09093		
		4.354	0.17797		
		4.250	0.24093		

<sup>1</sup> Osaka, *Z. physik. Chem.*, 41, 560 (1902).

The freezing-point lowerings of equimolar solutions of sodium and potassium sulfate and of sodium sulfate were measured. The values for potassium sulfate were taken from the work of Hall and Harkins.

The concentration of the mixture was calculated on the basis of the average molecular weight. The curve, Fig. 1, shows  $\Delta t/N$  plotted against the cube root of the concentration.

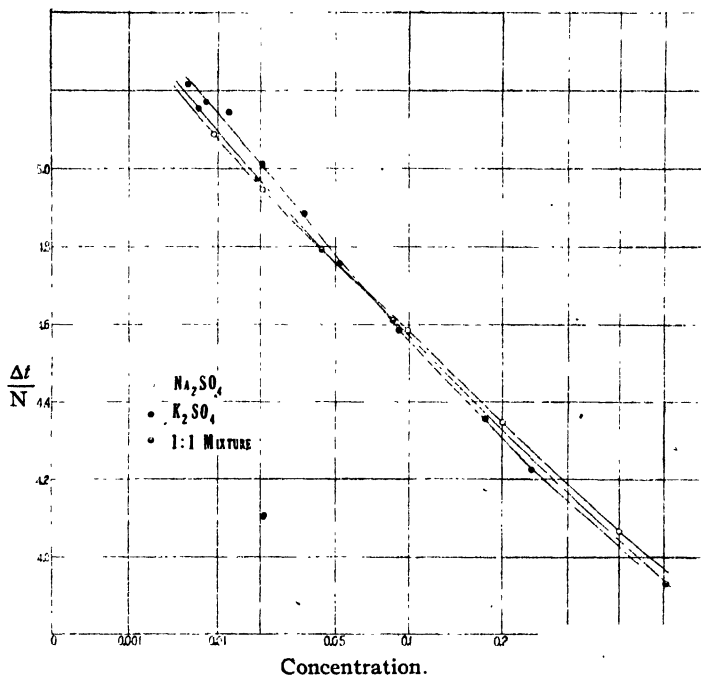


Fig. 1.—Freezing-point lowerings for two uni-bivalent salts and for their 1:1 mixture.

The results indicate that in the case of these two uni-bivalent salts the lowering of the freezing point caused by the mixture is very nearly the average of the lowering of the two salts taken separately.

The lowering of the freezing points of solution of sodium chloride and of mixtures of sodium and potassium chloride were measured. The results indicated an exceptional lowering in the case of these mixtures. A mixture of 1 NaCl to 1 KCl showed a value of  $\Delta t/N$  below either NaCl or KCl at the more dilute points. A mixture of 2 NaCl to 1 KCl gives values between the 1:1 mixture and the values expected, if there is no effect of the one salt on the other. The numerical results will not be given as it is thought best to redetermine the values for these mixtures.

Table III gives the value for the sodium chloride alone.

TABLE III.—FREEZING-POINT DATA ON SODIUM CHLORIDE.

$\Delta t/N$ .	Concentration.
3.650	0.005132
3.623	0.009544
3.616	0.009604
3.561	0.02012
3.560	0.02120
3.534	0.03516
3.498	0.06534
3.435	0.08360
3.448	0.1360

### Summary.

This paper gives determinations of the freezing-point lowerings for solutions of sodium sulfate, potassium sulfate, and their equimolar mixture, for sodium chloride, and for a mixture of mannite and potassium chloride. The greatest temperature deviation to be found from the calculated value in the potassium-chloride-mannite mixture, was six one-hundred-thousandths of a degree.

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

## IONIZATION AND SOLUBILITY RELATIONS OF SALTS OF HIGHER TYPES.<sup>1</sup> IV.

### INTERMEDIATE IONS IN SOLUTIONS OF UNI-BIVALENT SALTS, AND OF LANTHANUM IODATE, A TRI-UNIVALENT SALT.

BY WILLIAM D. HARKINS AND W. TUDOR PEARCE.<sup>2</sup>

Received August 23, 1916.

### Introduction.

A survey of any general treatise on chemistry indicates that lower type salts, that is, those of the uni-univalent type, are few in number in comparison with salts of the higher types, yet the latter class of salts has received little attention from the standpoint of general ionization and solubility relations. So slight indeed is the attention paid

<sup>1</sup> The part of this work which bears directly upon uni-bivalent salts was done by Harkins in the Research Laboratory of Physical Chemistry of the Massachusetts Institute of Technology, and the importance of such an investigation was suggested by Dr. A. A. Noyes, who obtained financial support for the work from the Carnegie Institution of Washington. The first three papers on higher type salts (Papers V, VI and VII, The Effect of Salts upon the Solubility of Other Salts, *THIS JOURNAL* 33, 1807-73 (1911)) were largely experimental and did not give an adequate discussion of the theoretical relations involved in the intermediate ion hypothesis.

<sup>2</sup> This paper, and one published later in this series, have been presented to the University of Chicago by W. Tudor Pearce as a dissertation in part fulfilment of the requirements for the degree of Doctor of Philosophy. In addition to the work here presented, a considerable time was spent upon the separation of the yttrium group elements.

to higher type salts, that although it was shown in 1911 by Harkins<sup>1</sup> that all salts of the uni-bivalent type ionize in two steps, and thus give solutions containing intermediate ions, almost none of the recent texts on general, inorganic, or physical chemistry<sup>2</sup> even mention the possibility of the existence of intermediate ions. This of itself might not be so bad if these texts did not persist in giving the altogether false percentage ionizations which are obtained by calculation when the presence of intermediate ions is neglected. Thus in two well-known college text books published recently the percentage ionization of potassium sulfate in a tenth normal solution is given as 72%, even although the work cited above shows that in all probability more nearly 95% of a salt of this uni-bivalent type is in the ionic form at this concentration. Even if the authors of these texts do not believe that intermediate ions exist in appreciable quantities in solutions of such salts, the better method would be to express their results in terms of the conductance ratio without the application of the hypothetical term "degree of ionization."

Previous to the publication of the first papers of this series it had been suggested by a number of workers that intermediate salt ions were present in certain specific cases, but these suggestions were made to cover only what seemed to be extraordinary cases. Thus Abe $\ddot{g}$ g and Spencer<sup>3</sup> assumed that when thallium oxalate ionizes it forms intermediate ions, but that potassium oxalate does not. Also Jellinek<sup>4</sup> concluded from freezing-point results that intermediate ions are formed by sodium sulfate, but not by potassium sulfate. The new feature of the intermediate ion hypothesis is that it assumes that intermediate ions are present in solutions of all salts of higher types, and that the percentage amount of the intermediate ion increases regularly with the concentration, somewhat as the concentration of the un-ionized part of a lower type salt increases.

The most striking fact found by Harkins was that, while the solubility of a uni-bivalent salt is depressed in a normal way by the addition of a salt with a univalent ion, and while on the whole the action of a salt with a non-common ion is also normal, that when the common bivalent ion is added the effect on the solubility is extremely abnormal for very soluble salts and in concentrated solutions, and is still quite abnormal in dilute solutions, but becomes almost normal in solutions of extreme dilution. The effect found is that the decrease in solubility produced by the addition of a salt with a bivalent common ion is very much less than would be expected in dilute solutions, and in concentrated solutions there is often

<sup>1</sup> THIS JOURNAL, 33, 1807-73 (1911).

<sup>2</sup> Washburn's "Principles of Physical Chemistry" is an exception in this respect.

<sup>3</sup> *Z. anorg. Chem.*, 46, 406 (1905).

<sup>4</sup> *Z. physik. Chem.*, 76, 309 (1911).



even an *increase instead of a decrease* of solubility. Since salts which form complexes were avoided as much as possible in the experimental work, this behavior suggests what may be called a non-common ion effect. Now if strontium bromide and strontium nitrate in concentrated solutions were to ionize only to the extent of one step, the ions formed would be  $\text{SrBr}^+$  and  $\text{SrNO}_3^+$ ,  $\text{Br}^-$ , and  $\text{NO}_3^-$ . None of these is a common ion, and, therefore, from the standpoint of intermediate ions an increase of solubility is easily explainable.

There will now be considered the lowering of the solubility of a salt caused by the presence of (1) a common univalent ion, and of (2) a common bivalent ion. One calculation will be made assuming that intermediate ions are absent, and a second on the basis of the presence of such ions, and then a comparison of the results obtained in the two cases will be possible.

**1. Solubility Effects when Intermediate Ions are Absent.**—Let a salt  $\text{A}_2\text{B}$  ionize directly into  $2\text{A}^+$  ions and one  $\text{B}^-$  ion. Then, when formulated according to the mass law, and when  $\text{S}_0$  represents the solubility in water,  $\text{S}_1$  when the common univalent ion is added, and  $\text{S}_2$  when the common ion is bivalent, the following expressions are obtained:

$$(\text{A}_2\text{B})_0 = (\text{A}_2\text{B})_1 = (\text{A}_2\text{B})_2 \quad (1)$$

$$(\text{A})^2(\text{B})_0 = (\text{A})_1^2(\text{B})_1 = (\text{A})^2(\text{B})_2 \quad (2)$$

$$\text{S}_0 = (\text{A}_2\text{B})_0 + (\text{B})_0 \quad \text{S}_1 = (\text{A}_2\text{B})_1 + (\text{B})_1 \quad (3)$$

$$2\text{S}_0 = 2(\text{A}_2\text{B})_0 + \text{A}_0 \quad (4) \quad 2\text{S}_2 = 2(\text{A}_2\text{B})_2 + (\text{A})_2 \quad (5)$$

By combining these equations results may be obtained which represent the fractional decrease of solubility produced by increasing the concentration of the univalent ion from  $(\text{A})_0$  to  $(\text{A})_1$ , and of the bivalent ion from  $(\text{B})_0$  to  $(\text{B})_2$ :<sup>1</sup>

$$\text{S}_0 - \text{S}_1 = \frac{(\text{A})_1 - (\text{A})_0}{(\text{A})_0} \left[ \frac{\text{A}_0\text{B}_0}{\text{A}_1} \left( 1 + \frac{\text{A}_0}{\text{A}_1} \right) \right] \quad (6a)$$

$$\text{S}_0 - \text{S}_2 = \frac{1}{2} \frac{(\text{B})_2^{1/2}(\text{B})_0^{1/2}}{(\text{B})_0^{1/2}} \left\{ (\text{A})_0 \left[ \frac{(\text{B})_0}{(\text{B})_2} \right]^{1/2} \right\} \quad (7)$$

Equation 6a may be more simply expressed as follows:

$$\text{S}_0 - \text{S}_1 = \frac{(\text{A})_1 - (\text{A})_0}{(\text{A})_1} \left[ (\text{B})_0 \left\{ 1 + \frac{(\text{A})_0}{(\text{A})_1} \right\} \right]$$

<sup>1</sup> These calculations made on the basis of the law of mass action will be somewhat in error, since the principle that the concentration of the un-ionized part remains constant seems to be considerably in error if we judge from the behavior of uni-univalent salts, but the effect of the error on the result in case intermediate ions are present is exceedingly slight, since the concentration of the un-ionized part is very small in proportion to the total concentration. There is also some deviation from the solubility product principle, but this deviation is slight and the resultant error is in the opposite direction from the first one mentioned.

From these equations it would be expected that the addition of the common univalent ion would in all cases effect a considerable lowering in the solubility. The addition of the common bivalent ion would also produce a considerable effect of the same kind, though slightly smaller in magnitude.

**2. Solubility Effects when Intermediate Ions Are Present.**—When intermediate ions are present Equations 6 and 7 take the form

$$S_0 - S_1 = \frac{(A)_1 - (A)_0}{(A)_1} \left[ (B)_0 \left( 1 + \frac{(A)_0}{(A)_1} \right) + (AB)_0 \right] \quad (6b)$$

$$S_0 - S_2 = \frac{1}{2} \frac{(B)_2^{1/2} - (B)_0^{1/2}}{(B)_0^{1/2}} \left[ (A)_0 \left( \frac{(B)_0}{(B)_2} \right)^{1/2} - (AB)_0 \right] - (ADB)_2 \quad (7b)$$

However, in Equations 6b and 7b the values of the concentrations are very different from what they are in Equations 6 and 7

The positive sign of the term  $(AB)_0$  in Equation 6b shows that the effect of the presence of the intermediate ion is to make the *decrease* of solubility larger, and the effect of this term increases with the percentage of the intermediate ion. The experimental results show that curves of this type exhibit this effect, and especially with salts like lead chloride and calcium hydroxide, which contain in solution an exceptionally large percentage of the intermediate ions. The curves for these salts, and also for lead iodate fall below the theoretical limiting curve for this type in the more dilute solutions. \* (Fig. 1.) The theoretical limiting curve is calculated for a salt of 100% ionization, which means that the presence of intermediate ions is not considered.

The negative signs on the terms  $(AB)_0$  and  $(ADB)_2$  indicate that when intermediate ions are present the decrease in solubility would be much less than that calculated on the basis that they are not present, which is exactly in accord with the experimental results. However, with a slightly soluble salt to which the bivalent common ion is added, the effect of the presence of the intermediate ion will not be specially noticeable, so long as the concentration of the added bivalent ion  $(B)_2$  is not greatly increased, since in this case the ratio of  $(AB)_0$  to  $A_0 B^{1/2} / B_2^{1/2}$  is small.

The decrease in solubility with this type of curve will change over into an increase when with a moderately soluble salt the concentration of the added salt is moderately increased for in this case the ratio  $(AB)_0 / A$  is fairly large and the negative term  $(AB)_0$  will soon compensate the steadily decreasing positive term containing  $(A)_0$  to so great an extent that the whole latter term of Equation 7b becomes negative, and this occurs all the sooner since the negative term  $(ADB)_2$  is constantly increasing.

When either the saturating salt is very soluble, or contains a specially large percentage of intermediate ion, even the first addition of a salt with a common bivalent ion may cause an increase in solubility, for where

$(AB)_0/(A)_0$  is sufficiently large the two negative terms may exceed the positive one, even when the factor of the latter  $B_0^{1/2}/B_2^{1/2}$  is equal to unity. The general agreement of these equations, derived on the supposition that intermediate ions are present, with the experimental facts, is a strong argument in favor of the existence of intermediate ions.

**3. Evidence against the Intermediate Ion Hypothesis.**—The purpose of the present paper is to add experimental evidence which bears on the ionization of tri-univalent salts to that which has already been obtained in the case of salts of the uni-bivalent type. In studying such a problem it may be well to outline the evidence which has in the past seemed to indicate that intermediate ions do not exist in solutions of the latter type, and for this purpose there is cited a quotation from a paper by Noyes and Bray<sup>1</sup> as follows: "In the case of salts of the uni-bivalent type, there is furthermore the uncertainty as to whether intermediate ions (such as  $KSO_4^-$  or  $\cdot NO_3Ba^+$ ) are present in considerable proportions. Certain remarkably simple principles have, however, been established, which have been thought to indicate that the complications which would arise from ionization in two successive stages do not exist, namely: 1. The conductance ratio of such salts changes with the concentration according to the same exponential law  $(C\gamma)^n/C(1-\gamma) = K$  that holds in the case of uni-univalent salts. 2. The conductance of mixtures of such salts can be approximately calculated from the conductance of the constituents by the same principle expressed by the equation 
$$\left[ \frac{C_{B^+} \times C_{A^-}}{C_{BA}} = K(C\gamma)^{2-n} \right]$$

that holds for univalent salts. 3. The transference numbers of uni-bivalent salts (except those of the bivalent metal halides) change only slightly with increasing concentration. 4. Simple mixed salts (such as  $BaClNO_3$ ) scarcely ever separate in the solid state when solutions of the constituent salts are evaporated." In order that this quotation may not be misunderstood it may be said that in spite of the above evidence, the paper from which it is taken seems to favor rather than oppose the idea that intermediate ions exist.

**4. Conditions under Which the Objections Become Invalid.**—The very fact that the same equation

$$C_B \times C_{A^-}/C_{BA} = K(C)^{2-n} = K(\Sigma i)^q \quad (1)$$

which is found valid for the conductance ratios of single uni-univalent salts and which may also be used to calculate the conductance of mixtures of such salts, may be applied to salts of higher types without any essential change, should at once suggest that this equation, and other modified equations of this general type, are after all nothing more than they pretend to be, that is, entirely empirical equations which are valuable in

<sup>1</sup> THIS JOURNAL, 33, 1645 (1911).

connection with calculations of conductance and of conductance ratios, but which, at least in the case of salts of higher types, are not directly related to the ionization. Thus, if the above equation is valid for the ionization of the simple type salts, for those of the uni-bivalent type the equation should be of the form

$$\frac{C_B^2 \times C_{A^+}}{C_{B_2A}} = K (\Sigma i)^q \quad (2)$$

in case intermediates do not exist, and this latter equation would not change at all into the form of Equation 1 if intermediate ions are present.

Perhaps the most serious objection to the intermediate ion hypothesis is that given above under number (3), that the transference numbers of the uni-bivalent salts, except those of the bivalent metal halides, change only slightly with the concentration, even although the concentration of the intermediate ion if it is present, should increase rather rapidly with the concentration, at least in all cases where complex ions are not present. The fact is, from the experimental standpoint, that extensive researches on the transference numbers of potassium sulfate, barium nitrate,<sup>1</sup> and upon thallous sulfate and lead nitrate,<sup>2</sup> show that the change of the transference number with the concentration is very small, at least between 0.03 and 0.10 normal; in fact, there was no detectable change greater than might result from experimental errors. As a result of this work Falk comes to the following conclusion: "Some degree of probability therefore attaches to the hypothesis that such tri-ionic salts do not as a rule give rise to intermediate ions, at any rate in quantity exceeding a few per cent. at 0.1-0.2 normal; but that they dissociate directly into three ions. At any rate the statement can be made with positiveness that the transference relations of the tri-ionic salts afford no indication of the presence of intermediate ions, but whether this is due to the nonexistence of such ions or to the fact that they have a conductance of such magnitude as not to influence the transference, cannot be definitely stated."

In this connection it should be noticed that the transference method is by no means sufficiently accurate so that conclusions based upon transference results could be looked upon as at all conclusive, especially where the ions investigated have not very different speeds. In sulfuric acid, where the ions  $H^+$ ,  $HSO_4^-$  and  $SO_4^{2-}$  have greatly different velocities, the intermediate ion has been detected by transference measurements.

**5. Transference Number of Intermediate Ion.**—The necessary relation between the migration values of the different ions in order that the existence of the intermediate ion may escape detection, may easily be calculated. Thus for potassium sulfate the existence of the intermediate

<sup>1</sup> A. A. Noyes, *THIS JOURNAL*, 23, 37 (1901).

<sup>2</sup> Falk, *Ibid.*, 32, 1555 (1910).

ion must not very greatly alter the transference number of the potassium ion as it is calculated on the supposition that no intermediate ion is present. In a general form the equations are given below, where  $T_o$  represents the transference number when no intermediate ion is present, and  $T_i$  gives its value if the intermediate ion is present, and when the ionization occurs only for the first step. Now for a salt  $A_2B$

$$T_{oA+} = \frac{\Lambda_{A+}}{\Lambda_{A+} + \Lambda_{B-}} \quad (3)$$

$$T_{iA+} = \frac{\Lambda_{A+} - \Lambda_{AB-}}{\Lambda_{A+} + \Lambda_{AB-}} \quad (4)$$

Now if  $T_{oA+} = T_{iA+}$

$$\frac{\Lambda_{A+}}{\Lambda_{A+} + \Lambda_{B-}} = \frac{\Lambda_{A+} - \Lambda_{AB-}}{\Lambda_{A+} + \Lambda_{AB-}} \quad (5)$$

or  $\Lambda_{AB-} = \Lambda_{A+} \times \Lambda_{B-} / 2\Lambda_{A+} + \Lambda_{B-}$ . (6)

Equation 6 expresses the exact relationship which would absolutely prevent the detection of the intermediate ion, but since the transference method is not a very sensitive indicator in the case of salts, the conductance of the intermediate ion might vary considerably from this value without causing any very noticeable change in the transference number ( $T_A$ ) with the concentration.

If it is assumed that when the ions  $A^+$  and  $B^-$  unite to form the intermediate ion  $AB^-$ , the resistance to the motion of the intermediate ion is equal to that of its constituent ions, or  $R_{AB-} = R_{A+} + R_{B-}$ , then the equation for its conductance would be

$$\Lambda_{AB-} = \frac{I}{R_{AB-}} = \frac{I}{R_{A+} + R_{B-}} = \frac{I}{I/\Lambda_{A+} + I/\Lambda_{B-}} = \frac{\Lambda_{A+} \times \Lambda_{B-}}{2\Lambda_{A+} + \Lambda_{B-}}, \quad (7)$$

which is the same as Equation 6. So the condition necessary in order that the intermediate ion may have no influence upon the transference number is that the resistance to motion of the intermediate ion shall be equal to the sum of the resistance of its component ions.

**6. The Union of the Ions in Intermediate Ions and Probably in Molecules of Salts in Aqueous Solutions is a Loose One.**—It has been pointed out by G. N. Lewis that in the case of intermediate salt ions this condition should be very nearly fulfilled, since the properties of salts in solution are additive properties of the constituent ions, and the heat of ionization is small, so that the union of the ions is a loose one. On the other hand, the heat of ionization of the dibasic acids is considerable, and therefore in the case of such intermediate ions as  $HSO_4^-$  the above relationship would not hold, and such ions should be detected by transference measurements, as is the case. Not only is this true but the great differences in the

migration values of the constituent ions of such intermediate ions make the experimental detection of these ions by transference measurements much more feasible.

In spite of the failure of previous attempts to prove the presence of intermediate salt ions by transference measurements, it is not improbable that some evidence of their existence might be obtained by using salts of higher types in which one ion has a far greater migration value than the other, which might be done by loading up one of the ions with heavy organic radicals. However, the fact that such a method at the best would not prove a very sensitive one, makes it advisable to turn to other experimental methods.

A consideration of the migration values of some of the ions of salts of higher types will give some specific idea of the reasonableness of such an hypothesis in regard to the migration values of the ions. In the special case where these values are the same for both of the simple salt ions, Equations 5 and 6 give the result that the migration number of the intermediate should be one-third that of the constituent ions; or

$$\Lambda_{AB^-} = \frac{1}{3}\Lambda_{B^-} = \frac{1}{3}\Lambda_{A^+}. \quad (19)$$

In the case of potassium sulfate at 25°,

$$\Lambda_{SO_4^{2-}}/2 = 80.0, \Lambda_{K^+} = 74.8 \text{ and } \Lambda_{KSO_4^-} = 26.$$

Since the  $SO_4^{2-}$  ion if it had one charge could be pulled only one-half as fast, the migration value would be 40. The potassium would still further load up the  $KSO_4^-$  ion, and thus increase its resistance. So that the decrease of the migration value from 40 to anywhere near 26 must be due to the resultant increase in size of the ion.

**7. The Intermediate Ion Hypothesis.**—The intermediate ion hypothesis, as proposed by Harkins in 1911, but not that time emphasized, may be stated as follows: (1) All salts, acids and bases which dissociate electrolytically into more than two ions, dissociate in steps, and thus form in solution intermediate ions. (2) These intermediate ions are present in dilute as well as in concentrated solutions, but the percentage of the salt present as intermediate ion decreases as the solution becomes more dilute.

When the intermediate salt ions, such as  $KSO_4^-$ , are compared with the corresponding intermediate acid ions, such as  $HSO_4^-$ , it is found that the intermediate salt ion has in general the higher ionization constant. It is well known that the intermediate ion of a strong acid ( $HSO_4^-$ ) has a moderately high ionization constant, but that this constant is extremely small in the case of the weak acids ( $HCO_3^-$ ). Undoubtedly the same relations are true for the intermediate ions of bases. The ionization of intermediate salt ions differs from that of the similar ions in acids and bases, somewhat as the ionization of uni-univalent salts differs from that of acids and bases;

that is, the ionization constants are in all cases relatively high in the case of salts (with of course such exceptions as occur in cadmium and mercury salts, which have a high tendency toward complex formation). However, the ionization constants of intermediate salt ions are not so high as to make these ions negligible in solutions of ordinary concentration.

**8. Calculation of the Percentage of Intermediate Ions and Other Constituents in Solutions of Higher Type Salts.**—The greatest difficulty which we encounter when an endeavor is made to calculate the percentage of intermediate ion present in the solution of a higher type salt, is that we do not as yet know how to calculate the percentage ionization of a salt of the simplest type. If we assume that the value of the conductance ratio, or of the conductance ratio modified by some function of the viscosity, gives the correct values for the ionization of simple type salts, then it is possible without the introduction of assumptions which are any more doubtful than those used in this simple case, to calculate the ionization of salts of the uni-bivalent type.

In order that comparisons may be made between the ordinary system of calculating the ionization of tri-ionic salts, and that which takes account of the existence of intermediate ions, and also so that the similar relations for uni-trivalent salts may be understood, the results of calculations of this kind will be given.

There are two assumptions which seem to afford the best basis for estimating the proportions of the constituents in solutions of uni-bivalent salts. The first of these is the assumption that the principle that different salts of the same valence type have approximately the same ionization values, or more properly the same ionization constants,<sup>1</sup> applies to the first stage of the ionization of uni-bivalent salts. Thus if a salt  $A_2B$  (such as  $Ag_2SO_4$ ) ionizes at first into  $A^+ + AB^-$ , it ionizes as a uni-univalent salt, and should therefore be about 83% ionized in this way in 0.1 normal solution.

The second assumption is based on the fact that the transference numbers of uni-bivalent salts (excluding the halides of bivalent metals) vary scarcely at all with the concentration. As has been shown, it is a necessary consequence of this fact that the intermediate ion, if it be present in considerable quantity, has an equivalent conductance equal to  $\Lambda_A \Lambda_B / (2\Lambda_A + \Lambda_B)$  where  $\Lambda_A$  and  $\Lambda_B$  are the equivalent conductances of the simple univalent and bivalent ions of a salt,  $A_2B$ . The method used was to calculate by a method of approximations the concentrations of the constituents which under the assumptions just stated cause the calculated specific conductance of the solution in each case to be the same as that experimentally determined. The results are given in Table I.

<sup>1</sup> Noyes, *THIS JOURNAL*, 30, 351 (1908).

TABLE I.—CONCENTRATIONS OF THE INTERMEDIATE ION AND OF THE OTHER CONSTITUENTS IN SOLUTIONS OF UNI-BIVALENT SALTS WITH THE ORDINARY VALUES GIVEN IN PARENTHESIS.

Silver Sulfate.						
Equiv. conc. of salt.	0.01	....	0.05352	....	0.10	....
Conc. Ag = $\Sigma i$ ....	0.00878	(0.00836)	0.0403	(0.03035)	0.0702	(0.0617)
AgSO <sub>4</sub> .....	0.00107	....	0.01004	....	0.02186	....
SO <sub>4</sub> =.....	0.00385	(0.00418)	0.01513	(0.01823)	0.02417	(0.03085)
Ag <sub>2</sub> SO <sub>4</sub> .....	0.000077	(0.00082)	0.001596	(0.00853)	0.00397	(0.0191)
$k_1 = \frac{[Ag^+][NO_3^-]}{[AgNO_3]}$	0.123	....	0.254	....	0.336	....
$k_2 = \frac{[Ag^+][SO_4^{--}]}{[AgSO_4^-]}$	0.0316	....	0.0608	....	0.0776	....
Per cent. sulfate as						
AgSO <sub>4</sub> <sup>-</sup> .....	21.4	....	37.50	....	43.7	....
SO <sub>4</sub> =.....	77.0	(83.6)	56.5	(68.1)	48.3	(61.7)
Ag <sub>2</sub> SO <sub>4</sub> .....	1.54	(16.4)	5.97	(31.9)	7.94	(38.3)
Total mols.....	0.01447	(0.01336)	0.06707	(0.06321)	0.1202	(0.1116)
Potassium Sulfate.						
Equiv. conc. of salt.	0.01	....	0.10	....	1.00	....
Conc. K = $\Sigma i$ .....	0.0090	(0.00869)	0.0774	(0.0710)	0.62	(0.592)
KSO <sub>4</sub> .....	0.0009	....	0.0176	....	0.25	....
SO <sub>4</sub> .....	0.00405	(0.004345)	0.0299	(0.0355)	0.185	(0.296)
K <sub>2</sub> SO <sub>4</sub> .....	0.00005	(0.000655)	0.0025	(0.0145)	0.165	(0.204)
$k_1 = \frac{[K^+][Cl^-]}{[KCl]}$	0.150	....	0.533	....	2.32	....
$k_2 = \frac{[K^+][SO_4^{--}]}{[KSO_4^-]}$	0.040	....	0.132	....	0.46	....
Per cent. sulfate as						
KSO <sub>4</sub> <sup>-</sup> .....	18.0	....	35.2	....	46.0	....
SO <sub>4</sub> =.....	81.0	(86.9)	59.8	(71.0)	42.0	(59.2)
K <sub>2</sub> SO <sub>4</sub> .....	1.0	(13.1)	5.0	(29.0)	12.0	(40.8)
Total mols.....	0.01400	(0.01369)	0.1274	(0.1210)	1.220	(1.092)
Sodium Sulfate. <sup>1</sup>						
Equiv. conc. of salt..	0.02	....	0.10	....	0.20	....
Conc. Na = $\Sigma i$ .....	0.01722	....	0.07640	....	0.1415	....
NaSO <sub>4</sub> <sup>-</sup> .....	0.00234	....	0.01732	....	0.03950	....
SO <sub>4</sub> =.....	0.00744	....	0.02954	....	0.051	....
Na <sub>2</sub> SO <sub>4</sub> .....	0.00022	....	0.00314	....	0.0095	....
$k_1 = \frac{[Na^+][SO_4^{--}]}{[Na_2SO_4]}$	0.18316	....	0.42142	....	0.58825	....
$k_2 = \frac{[Na^+][SO_4^{--}]}{[NaSO_4^-]}$	0.05475	....	0.13030	....	0.1827	....
Per cent. sulfate as						
NaSO <sub>4</sub> <sup>-</sup> .....	23.40	....	34.64	....	39.5	....
SO <sub>4</sub> <sup>=</sup> .....	74.4	....	59.08	....	51.0	....
Na <sub>2</sub> SO <sub>4</sub> .....	2.2	....	6.28	....	9.5	....

<sup>1</sup> Calculated for us by Dr. S. D. Wilson.



It will be seen from this table that the proportion of intermediate ion increases rapidly with increasing concentration. The most striking result, however, is that  $K_2$ , the ionization function for the second stage of ionization, increases with increasing ion concentration, and is nearly proportional to  $K_1$ .

The assumption used in the calculation of the first step of the ionization of a tri-ionic salt was that usually adopted for salts of the simplest type, that is, that the conductivity ratio, or the conductivity ratio modified by a function of the viscosity, gives the ionization. When such an assumption is made, it is found empirically that the Storch<sup>1</sup> equation

$$\frac{\Lambda_0 - \Lambda}{\gamma \Lambda_0} = k \left( \frac{\Lambda}{\Lambda_0} \right)^x$$

or in its modified form as given by Bancroft<sup>2</sup>

$$C_2^n / C_3 = K$$

expresses the relations which are found, where  $N = 2 - f(K)$ , where  $f(K)$  varies approximately between 0 and  $1/2$ . The latter equation is now often used in the following forms:

$$\frac{(C\gamma)^2}{C(1-\gamma)} = K_1(C\gamma)^{2-n}, \quad \frac{(C\gamma)^2}{C(1-\gamma)} = k_1(\Sigma i)^{2-n} \quad \text{or} \quad \frac{C_{B^+} \times C_{A^-}}{C_{BA}} = k_1(\Sigma i)^{2-n}.$$

Since the value of  $k(\Sigma i)$  becomes 0 at zero concentration, it has been proposed by Kraus,<sup>3</sup> and by Kraus and Bray that an additional constant be inserted, which gives the equation the following form when the viscosity correction is included:

$$(C\gamma/\eta\eta_0)^2 / C(1-\gamma/\eta\eta_0) = k + k_1(C\gamma/\eta\eta_0)^h$$

which is perhaps better expressed:

$$\frac{(\Lambda\eta/\Lambda_0\eta_0)^2 C}{(1-\Lambda\eta/\Lambda_0\eta_0)} = k + k_1 \left( C \frac{\Lambda\eta}{\Lambda_0\eta_0} \right)$$

However the simpler form of the equation gives sufficiently accurate results for highly ionized substances in aqueous solution at the concentrations given in Table I, so this simpler form has been used in the calculation, which would otherwise be extremely involved. The results of these calculations show that when it is assumed that the first step in the ionization follows the usual rule of the uni-univalent salts, the second step follows a similar rule, but with a much smaller value of  $K(\Sigma i)^{2-n} = K_2$ .

**9. Values of the Exponent  $n$  for the Steps in the Ionization of the Tri-ionic Salt Silver Sulfate.**—It is interesting in this connection to calculate the values of  $n$  in the equations which fit the different steps in the ionization.

<sup>1</sup> Storch, *Z. physik. Chem.*, **19**, 13-19 (1894).

<sup>2</sup> *Ibid.*, **31**, 189 (1899).

<sup>3</sup> *THIS JOURNAL*, **35**, 1412 (1913).

Normal concn.	First step. $\text{Ag}_2\text{SO}_4 = \text{Ag AgSO}_4^{-n_1}$	Second step. $\text{AgSO}_4 = \text{Ag SO}_4^{n-n_1}$
0.01 to 0.05	1.52	1.57
0.05 to 0.10	1.49	1.56

This shows that an equation of the Storch form also fits the second step in the ionization of salts of the tri-ionic type.

The equations for these two steps may be given as follows:

$$\frac{C_{B^+} \times C_{AB^-}}{C_{B_2A}} = K' (\Sigma i)^{2-n_1} \quad (1)$$

$$\frac{C_{B^+} \times C_{A^-}}{C_{BA^-}} = K'' (\Sigma i)^{2-n_2} \quad (2)$$

or combined in one equation:

$$\frac{C_{B^+}^2 \times C_{A^-}}{C_{B_2A}} = K'K'' (\Sigma i)^{4-n_1-n_2} \quad (3)^1$$

For silver sulfate:

$$\frac{C_{B^+}^2 \times C_{A^-}}{C_{B_2A}} = K'K'' (\Sigma i)^{0.94} = K (\Sigma i)^{0.94}$$

So approximately  $\frac{C_{B^+} \times C_{A^-}}{C_{B_2A}} = K_i$ , for this salt, where  $K_i$  is a real constant.

The results given in Table I are compared with those obtained by Noyes and Eastman<sup>2</sup> in Table II.

TABLE II.—COMPARISON OF THE IONIZATIONS OF SULFURIC ACID AND OF POTASSIUM SULFATE, CALCULATED FROM THE STANDPOINT OF THE EXISTENCE OF INTERMEDIATE IONS.

	Salt.	Acid.	Salt	Acid.
Equiv. concn.....	0.01	0.01	0.1	0.1
Formal concn.....	0.005	0.005	0.05	0.05
$K^+$ or $H^+ = \Sigma i$ .....	0.0090	0.0081	0.0774	0.0625
$\text{KSO}_4^-$ or $\text{HSO}_4^-$ .....	0.0009	0.0017	0.0176	0.0315
$\text{SO}_4^{2-}$ .....	0.00405	0.0032	0.0299	0.0155
$\text{K}_2\text{SO}_4$ or $\text{H}_2\text{SO}_4$ .....	0.00005	0.00010	0.0025	0.0030
$K_1 = A^+ \times AB^-/AB_2$ .....	0.150	0.138	0.553	0.626
$K_2 = A^+ \times B^-/AB^-$ .....	0.040	0.0152	0.132	0.0307

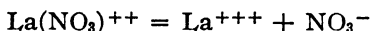
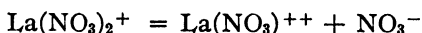
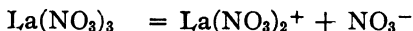
It will be seen that the first ionization constant obtained ( $K_1$ ) is nearly the same for the salt or the acid at the same concentration, but that the ionization constant of the intermediate ion ( $K_2$ ) is much smaller for the acid ion than for the salt ion, which is in accord with the idea presented earlier in this paper. In all cases the second ionization constant ( $K_2$ ) is much smaller than the first (about  $1/4$  as much in the case of the salts),

<sup>1</sup> It must be remembered in applying this equation that the concentrations are not those usually used and are *not* equal to the conductance ratios, but are the concentrations given in Table I.

<sup>2</sup> Noyes and Eastman, *THIS JOURNAL*, 32, 1148 (1910).

as might be expected, since in the intermediate ion the univalent ion must separate from a doubly charged ion.

**10. The Ionization of a Tri-univalent Salt.**—The calculation of the concentration of the constituents in a solution of a tri-univalent salt, such as lanthanum nitrate or iodate has not been attempted, though it would be possible to make such a calculation. However, some additional assumptions would be introduced, and without making the calculations all of the general conclusions of value can be obtained by considering the results given in Table I. As compared with the uni-bivalent salt which on ionization forms only one intermediate ion, we would expect that in the uni-trivalent salt the percentage of univalent ion would be increased, the percentage of the ion of highest valence would be decreased, that of the molecules would be decreased, and the percentage of intermediate ion would be increased, since now there would be two intermediate ions instead of one. Thus lanthanum nitrate would ionize as follows:



**11. Discussion of the Valence-Product Rule.**—From the standpoint of the above paragraph it may be said that for uni-univalent, uni-bivalent, and uni-trivalent salts, *the total percentage amount of salt in the ionic form increases with the valence product*, which is just the opposite of the rule which has been considered valid in the past.<sup>1</sup> Also when these salts are taken in the same order, the percentage of un-ionized salt decreases, which is again the opposite of the usual rule.

An inspection of Table I will show that the total number of particles (mols) present is not very greatly different when allowance is made for the presence of intermediate ions from that usually calculated when they are supposed to be absent. Thus in *N*/10 potassium sulfate the total number of mols is 0.1274 on the intermediate ion basis, and 0.1210 from the ordinary standpoint, so that the former method gives only a slightly larger number than the latter. When the number of ions is calculated for the same solution, the values are 0.1249 and 0.1065, respectively, so that many more ions are present from the intermediate ion standpoint. If 0.1 normal (0.05 molar) potassium sulfate were to completely dissociate it would give 0.15 mol of ions, so that with the intermediate ions present we have 83.3% of the possible number of ions instead of 71% as usually calculated. However, only 5% of the salt remains in the un-ionized form, so 95% is in the form of ions. There is no real contradiction in these values, but only an apparent one, due to the fact that the intermediate ions are intermediate in composition between the un-ionized molecules and the ions which result from complete ionization.

<sup>1</sup> Noyes and Johnston, *THIS JOURNAL*, 31, 1002 (1909).

Since a salt of the uni-univalent type gives at tenth normal concentration only 85% of the total possible number of ions, and as seen above, a uni-bivalent salt gives about 83% of the possible number at the same normal concentration, there is not much difference between the ionization of the two types of salts when they are looked at from just this standpoint.

When the ionization of a higher type salt is calculated without reference to the presence of intermediate ions, the relations are found to be expressed by the valence-product rule, that the ionization decreases rapidly when the product of the valences of the constituent ions increases. This relation is shown in Table III.

TABLE III.—VALUES OF THE CONDUCTANCE RATIO (OR IONIZATION IF THE PRESENCE OF INTERMEDIATE IONS IS NOT TAKEN INTO ACCOUNT) IN RELATION TO VALENCE TYPE.

Salt.	Valence product.	Conductance ratio $\times 10^3$ in 0.1 <i>N</i> soln. at 18°.
KCl	$1 \times 1 = 1$	86
KNO <sub>3</sub>		83
NaCl		84
AgNO <sub>3</sub>		81
NaC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>		83
K <sub>2</sub> SO <sub>4</sub>	$1 \times 2 = 2$	72
Na <sub>2</sub> SO <sub>4</sub>		70
Ca(NO <sub>3</sub> ) <sub>2</sub>		73
Ba(NO <sub>3</sub> ) <sub>2</sub>		68
La(NO <sub>3</sub> ) <sub>3</sub>	$3 \times 1 = 3$	65
K <sub>3</sub> C <sub>6</sub> H <sub>5</sub> O <sub>7</sub>		65
K <sub>4</sub> Fe(CN) <sub>6</sub>	$1 \times 4 = 4$	53

Noyes and Johnston find that these results can be expressed in another form, in which they show that there is an approximate proportionality between the un-ionized *fraction* of a salt and the valence product, when no allowance is made for the existence of intermediate ions in the solution. It seems that the idea which led to the expression of the results in the latter form was undoubtedly that as the valence product increases the electrical forces tending to hold the ions together increase, and therefore, from a theoretical standpoint the un-ionized fraction should increase. From the intermediate ion standpoint, however, while the above rules still apply to the conductance ratio, they no longer apply to the ionization, since, as has been stated above, the ionized fraction seems to increase and the un-ionized fraction to decrease as the valence product increases if the salts are of the 1,1; 1,2; or 1,3 types. However, that the idea from which the valence-product rule was derived is itself correct is indicated by the ionization functions, often called ionization constants, for the two steps in the ionization of a uni-bivalent salt, as given by Table I. These show that the ionization is much greater for the first step where the two univalent ions separate according to the reaction  $B_2A = B^+ + BA^-$ ,

than when the univalent ion separates from the bivalent one,  $BA^- = B^+ + A^-$ , in fact the ionization function is only about one-fourth as large for the second reaction as it is for the first.

### Experimental Part.

**1. Introduction.**—In the first three papers dealing with intermediate ions, the solubility and conductivity results on a large number of uni-bivalent salts were presented. Perhaps the most striking experimental result obtained was that while the salts of this type behave quite normally as to the variation of their solubility when either (1) a salt with a common univalent ion, or (2) a salt with *no common ion* is added to the solution, the same is not true when (3) a salt with a common bivalent ion is added. In the latter case the effect is on the whole a normal one, with one exception which will be pointed out later, when the saturating salt is of extremely slight solubility, as was the case with lead iodate, solubility 0.00011-equivalent per liter at 25°. However, as the solubility of the saturating salt increases, the effect becomes more and more abnormal, until for very soluble salts the solubility curve for the common bivalent ion takes on the form of a curve representing the addition of a salt with no common ion. The generality of the result at once suggests that the effect is not due to complex salt formation, which is more specific in its action.

The experimental work in this paper will deal with the solubility effects in the case of a tri-univalent salt. In solutions of salts of this type it would be expected that any abnormalities found in the relations of the uni-bivalent salts would become more pronounced, that is, when the two types of salts are compared at the same concentration. In the work on uni-bivalent salts all practical ranges of solubility have been studied from 0.0001 to 8.6 equivalents per 1000 grams of water, a range expressed by a factor nearly equal to 10,000. It was desired that the tri-univalent salt chosen should be as little inclined toward complex formation as possible, and in order that the principal part of the data might be obtained in very dilute solutions, a very slightly soluble salt was desired. There are as a matter of fact very few salts which meet these specifications, and of these lanthanum iodate seemed to be the best adapted for the purpose. Other suitable salts were certain cobaltammines, but lanthanum iodate has the advantage that it is a more stable salt, and that its solution can be analyzed with extreme accuracy.

**2. Preparation of Salts and Solutions. Lanthanum Iodate.**—Hot dilute solutions containing lanthanum nitrate and potassium iodate were brought together, the former being in excess. The solution was stirred, and then quickly cooled by pouring into a vessel surrounded with ice. The precipitated salt was filtered, washed and *recrystallized* (a very tedious process in the case of such a slightly soluble salt) from conductivity water, with a maximum specific conductance of  $0.6 \times 10^{-6}$ . The slightly soluble salt was recrystallized in large evaporating dishes heated on steam baths. The

white salt on analysis gave the value of  $\text{La}_2\text{O}_3$  and iodine value as calculated from the formula  $\text{La}(\text{IO}_3)_3$ . Spectrographs made on a 6-in. Rowland concave grating showed the presence of no other rare earth.

**Lanthanum Nitrate.**—Crystals of the double nitrate of lanthanum and ammonium were obtained from the Welsbach Burner and Light Co., through the courtesy of Dr. H. S. Miner. These were recrystallized. A solution of the salt was made and the lanthanum precipitated as the oxalate, thoroughly washed and ignited in platinum dishes to the oxide. The lanthanum nitrate was then made by adding an excess of the oxide to nitric acid and crystallizing the salt from the clear solution. The salt was recrystallized from conductivity water.

All of the other salts used were chemically pure salts recrystallized from conductivity water. In making solutions and in diluting, conductivity water of the quality mentioned above was used.

The solubility was determined by the method formerly employed by Harkins in this kind of work.<sup>1</sup> At least four separate solubility determinations, two from undersaturation and two from supersaturation, were made for each.

**3. Methods of Analysis. Iodate.**—About fifty cc. of the saturated solution were quickly transferred from its container in the thermostat to a small weighed glass-stoppered Erlenmeyer flask. Two samples were taken from each bottle, making eight analyses for each determination of the solubility. The weighings were made at once, the solution transferred to a 700 cc. beaker and the flask rinsed until a volume of 400 cc. was obtained. Three cc. of concentrated hydrochloric acid were added, 5 grams of potassium iodide put in, and sodium thiosulfate was run in from a weight buret until the color of iodine had about disappeared. Then two cc. of a freshly made starch solution were added and the titration completed. The time for the titration was in each case three minutes.

The thiosulfate solution was made up with conductivity water and kept in a black bottle with a siphon attached. It was carefully standardized against resublimed iodine, pure recrystallized potassium iodate, and against a standard solution of potassium permanganate. For use as a reagent the stock solution, which was one-tenth normal, was transferred to another black bottle and diluted to ten times its volume.

**Lanthanum.**—(1) A weighed quantity of the solution was evaporated in a small weighed platinum dish or crucible in an air bath and ignited to the oxide. (2) The solution was diluted and the lanthanum precipitated as the oxalate. The oxalic acid was liberated and titrated in the usual way.

Table I gives the solubility of lanthanum iodate in water as 0.6842 gram per 1000 grams of water at 25°.

TABLE I.—SOLUBILITY OF LANTHANUM IODATE IN WATER AT 25°.  
(Concentrations in milliequivalents per liter.)

No.	Conc. $\text{La}(\text{IO}_3)_3$ .	Sp. cond. $\times 10^4$ .	Equiv. cond.	Density 25°.
1.....	3.0900	0.3066	99.206	0.998250
2.....	3.0904	0.3066	99.206	0.998251
3.....	3.0905	....	....	0.998251
4.....	3.0908	0.3066	99.206	0.998251
5.....	3.0902	....	....	0.9982505
6.....	3.0902	0.3066	....	0.9982505

**4. The Solubility of Lanthanum Iodate in Solutions of Lanthanum Nitrate, Potassium Iodate, Sodium Iodate, Sodium Nitrate and in Lanthanum Ammonium Nitrate.**—The results of these solubility determina-

<sup>1</sup> THIS JOURNAL, 33, 1811 (1911).

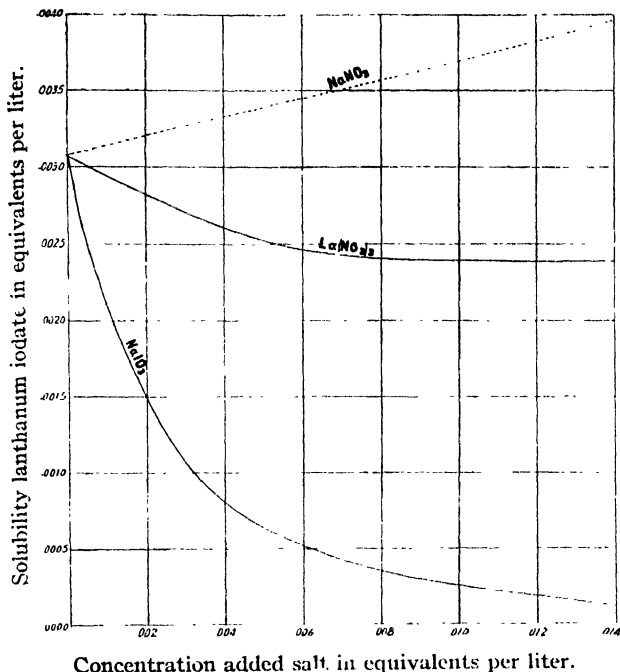


Fig. 1.—The solubility of the tri-univalent salt lanthanum iodate in very dilute solutions of other salts.

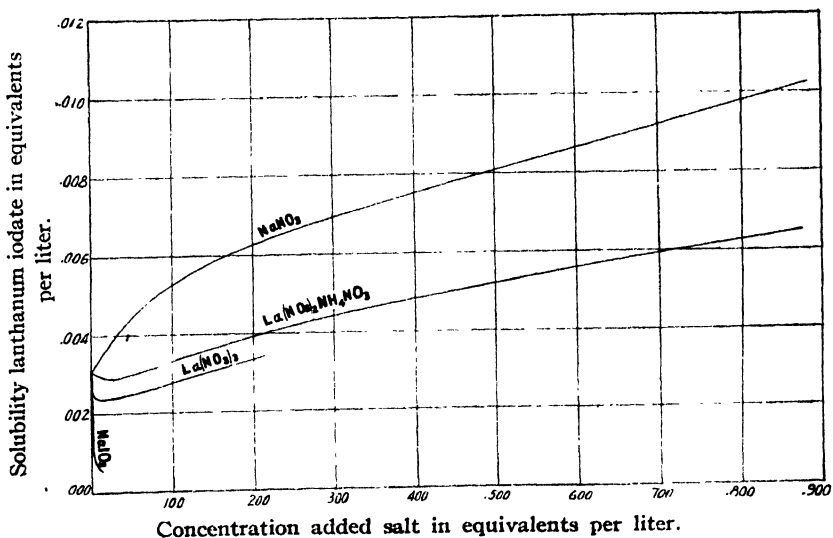


Fig. 2.—The solubility of lanthanum iodate in solutions of other salts. (For the dilute solutions see Fig. 1.)

tions are given in Table II. The mean values for the solubilities, with the solubility of the saturating salt expressed in millimols, are found in Table III together with the fractional concentrations of the added salt and the fractional solubility of lanthanum iodate. The "fractional conc. of added salt" is the ratio

$$\frac{\text{Equivalent conc. of added salt}}{\text{Equivalent solubility of the saturating salt}}$$

while the fractional solubility is the ratio

$$\frac{\text{Solubility of salt in salt solution}}{\text{Solubility of salt in water}}$$

These ratios are used for plotting the curves in Fig. 5. The solubility data presented in Table II are given in a graphic form in Figs. 1 and 2, where the ordinates represent the equivalent solubility of lanthanum iodate and the abscissae, the equivalent concentration of the added salts.

TABLE II.—SOLUBILITY OF LANTHANUM IODATE IN SALT SOLUTIONS AT 25°.  
(Concentrations in milliequivalents per liter.)

No.	Conc. added salt None.	Solubility La(IO <sub>3</sub> ) <sub>3</sub>	Mean solubility.	Solubility in grams per liter.	Sp. cond. X 10 <sup>4</sup> .	Density 25°/4°.
1.....	0.00000	.....	3.0904	0.6841	.....	0.998251
	La(NO <sub>3</sub> ) <sub>3</sub>					
7.....	2.00	2.529	.....	.....	.....	.....
8.....	.....	2.529s	.....	.....	.....	.....
9.....	.....	2.529	.....	.....	.....	.....
10.....	.....	2.529s	2.529	0.5595	0.4763	0.997323
11.....	5.00	2.390	.....	.....	.....	.....
12.....	.....	2.390s	.....	.....	.....	.....
13.....	.....	2.390	.....	.....	.....	.....
14.....	.....	2.390s	2.3905	0.5288	0.7991	0.998074
15.....	10.00	2.347	.....	.....	.....	.....
16.....	.....	2.347s	.....	.....	.....	.....
17.....	.....	2.347	.....	.....	.....	.....
18.....	.....	2.347s	2.3477	0.5194	1.3101	0.998590
19.....	50.00	2.496	.....	.....	.....	.....
20.....	.....	2.496s	.....	.....	.....	.....
21.....	.....	2.496	.....	.....	.....	.....
22.....	.....	2.496s	2.4960	0.5522	5.1076	1.002125
23.....	100.00	2.808s	.....	.....	.....	.....
24.....	.....	2.808	.....	.....	.....	.....
25.....	.....	2.808	.....	.....	.....	.....
26.....	.....	2.808s	2.8086	0.6214	9.286	1.006615
27.....	200.52	3.358	.....	.....	.....	.....
28.....	.....	3.358	3.3586	0.7431	16.752	1.015333
	KIO <sub>3</sub>					
29.....	0.099	2.843s	.....	.....	.....	.....
30.....	.....	2.843	.....	.....	.....	.....
31.....	.....	2.842	.....	.....	.....	.....
32.....	.....	2.842s	2.8430	0.6290	.....	1.00030



TABLE II (continued).

No.	Conc. added salt. None.	Solubility La(IO <sub>3</sub> ) <sub>3</sub> .	Mean solubility.	Solubility in grams per liter.	Sp. cond. $\times 10^4$ .	Density 25°/4°.
33.....	0.4957	2.546s	.....	.....	.....	.....
34.....	.....	2.546	.....	.....	.....	.....
35.....	.....	2.546	.....	.....	.....	.....
36.....	.....	2.546s	2.5464	0.5634	.....	1.000274
37.....	0.9914	2.246	.....	.....	.....	.....
38.....	.....	2.246s	.....	.....	.....	.....
39.....	.....	2.246	.....	.....	.....	.....
40.....	.....	2.246s	2.2465	0.4970	.....	1.00030
41.....	1.9828	1.689s	.....	.....	.....	.....
42.....	.....	1.689	.....	.....	.....	.....
43.....	.....	1.68975s	.....	.....	.....	.....
44.....	.....	1.68974	1.68974	0.37388	.....	1.000312
45.....	.....	.....	.....	.....	.....	.....
46.....	.....	.....	.....	.....	.....	.....
47.....	.....	.....	.....	.....	.....	.....
48.....	.....	.....	.....	.....	.....	.....
49.....	0.200	.....	(2.730)	.....	0.28033	.....
50.....	.....	.....	(2.540)	.....	0.30242	.....
51.....	.....	.....	(2.240)	.....	0.32740	.....
NaIO <sub>3</sub>						
52.....	0.0913	2.871	.....	.....	.....	.....
53.....	.....	2.872s	.....	.....	.....	.....
54.....	.....	2.871s	.....	.....	.....	.....
55.....	.....	2.871	2.8718	0.6353	.....	1.00060
56.....	0.4560	2.552s	.....	.....	.....	.....
57.....	.....	2.552	.....	.....	.....	.....
58.....	.....	2.552s	.....	.....	.....	.....
59.....	.....	2.552	2.5521	0.5646	.....	1.00059
60.....	0.9130	2.297s	.....	.....	.....	.....
61.....	.....	2.297	.....	.....	.....	.....
62.....	.....	2.297s	.....	.....	.....	.....
63.....	.....	2.297	2.2976	0.5083	.....	1.00065
64.....	1.8260	1.804	.....	.....	.....	.....
65.....	.....	1.805s	.....	.....	.....	.....
66.....	.....	1.804	.....	.....	.....	.....
67.....	.....	1.805s	1.8050	0.3993	.....	1.00065
68.....	3.6530	0.892s	.....	.....	.....	.....
69.....	.....	0.891	.....	.....	.....	.....
70.....	.....	0.891s	.....	.....	.....	.....
71.....	.....	0.892s	0.89200	0.1973	.....	1.00069
72.....	4.5326	0.6048	.....	.....	.....	.....
73.....	.....	0.6057	0.60530	0.1339	.....	1.00083
74.....	6.7989	0.4398	.....	.....	.....	.....
75.....	.....	0.4414s	0.44056	0.0973	.....	.....
NaNO <sub>3</sub>						
76.....	25.00	3.928s	.....	.....	.....	.....
77.....	.....	3.927	3.9277	0.8690	.....	1.00250

TABLE II (continued).

No.	Conc. added salt. None.	Solubility La(OH) <sub>3</sub> .	Mean solubility.	Solubility in grams per liter.	Sp. cond. $\times 10^3$ .	Density 25°/4°.
78.....	50.00	4.477 <sup>s</sup>	.....	.....	.....	.....
79.....	.....	4.475	4.4763	0.9904	.....	1.00385
80.....	100.00	5.244	.....	.....	.....	.....
81.....	.....	5.244 <sup>s</sup>	5.2443	1.160	.....	1.00742
82.....	200.00	6.263	.....	.....	.....	.....
83.....	.....	6.260 <sup>s</sup>	6.2619	1.385	.....	1.01290
84.....	400.00	7.396	.....	.....	.....	.....
85.....	.....	7.397 <sup>s</sup>	7.39717	1.636	.....	1.02422
86.....	800.00	9.741 <sup>s</sup>	.....	.....	.....	.....
87.....	.....	9.750	9.7462	2.156	.....	1.046775
88.....	1600.00	12.934 <sup>s</sup>	.....	.....	.....	.....
89.....	.....	12.934	12.9344	2.859	.....	1.09005
90.....	3200.00	13.697	.....	.....	.....	.....
91.....	.....	13.696 <sup>s</sup>	13.6972	3.030	.....	1.17243
92.....	1.00	(3.129)	.....	.....	0.41475	.....
93.....	2.00	(3.169)	.....	.....	0.52983	.....
94.....	10.00	(3.450)	.....	.....	1.41293	.....
La(NO <sub>3</sub> ) <sub>3</sub> ·2NH <sub>4</sub> NO <sub>3</sub>						
95.....	26.34	2.852	.....	.....	.....	.....
96.....	.....	2.854 <sup>s</sup>	.....	.....	.....	.....
97.....	.....	2.853	.....	.....	.....	.....
98.....	.....	2.852 <sup>s</sup>	2.853	.....	.....	1.001122
99.....	56.682	3.047 <sup>s</sup>	.....	.....	.....	.....
100.....	.....	3.048	.....	.....	.....	.....
101.....	.....	3.046	.....	.....	.....	.....
102.....	.....	3.047 <sup>s</sup>	3.047	.....	.....	1.003554
103.....	105.364	3.410	.....	.....	.....	.....
104.....	.....	3.410 <sup>s</sup>	.....	.....	.....	.....
105.....	.....	3.410	.....	.....	.....	.....
106.....	.....	3.410 <sup>s</sup>	3.4102	.....	.....	1.009711
107.....	158.048	3.691 <sup>s</sup>	.....	.....	.....	.....
108.....	.....	3.691	3.69105	.....	.....	1.016089
109.....	196.8375	3.918 <sup>s</sup>	.....	.....	.....	.....
110.....	.....	3.918	3.9184	.....	.....	1.021833
111.....	393.673	4.804	.....	.....	.....	.....
112.....	.....	4.805 <sup>s</sup>	4.8050	.....	.....	1.043438
113.....	787.35	6.165 <sup>s</sup>	.....	.....	.....	.....
114.....	.....	6.165	6.1554	.....	.....	1.08286
115.....	1574.70	8.690	.....	.....	.....	.....
116.....	.....	8.690 <sup>s</sup>	8.6904	.....	.....	1.16652

( ) = calc. from curve

s = equilibrium approached from supersaturation

### 5. Theoretical Limiting Solubility Curves for Various Type Salts.—

An examination of Figs. 1 and 2 shows that in the case of the tri-univalent salt, the addition of the common univalent ion gives the same form of curve as would be expected; that when a common trivalent ion is added the solubility decreases slightly, passes quickly through a minimum, and then

rapidly increases to a solubility greater than in water, with increasing concentration of the added salt. The rise of the curve in the latter case is far greater than would be the rise of a salt of the bi-univalent type of the same order of solubility. Fig. 2 shows the striking change of the curve from the type of the common ion to the one of the non-common ion.

TABLE III.—MEAN VALUES FOR THE SOLUBILITY OF LANTHANUM IODATE IN SOLUTIONS OF SALTS.

Salts added.	Milli-normal conc. salt solution.	Solubility in millimols.	Fractional conc. added salt.	Fractional conc. solubility.	Solubility grams per l.	Density 25°/4°.
La(NO <sub>3</sub> ) <sub>3</sub> .....	0.00	1.0301	0.0000	1.0000	0.6841	0.99825
	2.00	0.8430	0.6471	0.8183	0.5595	0.99732
	5.00	0.7968	1.6178	0.7733	0.5288	0.99807
	10.00	0.7825	3.2358	0.7596	0.5194	0.99859
	50.00	0.8320	16.1789	0.8076	0.5522	1.00212
	100.00	0.9362	32.3580	0.9088	0.6214	1.00661
	200.52	1.1195	64.8830	1.0868	0.7431	1.01533
KIO <sub>3</sub> .....	0.0000	1.0301	0.000000	1.0000	0.6841	0.99825
	0.0990	0.9476	0.032035	0.8785	0.6290	1.00030
	0.4957	0.8488	0.160175	0.8239	0.5633	1.00027
	0.9914	0.7488	0.320350	0.7269	0.4970	1.00030
	1.9828	0.5632	0.640700	0.5467	0.3738	1.00031
NaIO <sub>3</sub> .....	0.0000	1.0301	0.00000	1.0000	0.68410	0.99825
	0.0913	0.9572	0.02954	0.9292	0.63538	1.00060
	0.4560	0.8507	0.14771	0.8258	0.56466	1.00059
	0.9130	0.7658	0.29543	0.7434	0.50835	1.00065
	1.8260	0.6016	0.59086	0.5841	0.39938	1.00065
	3.6530	0.2973	1.18173	0.2886	0.19736	1.00069
	4.5326	0.2017	1.46670	0.1958	0.13393	1.00083
	6.7989	0.1468	2.20050	0.1425	0.09733	1.00130
NaNO <sub>3</sub> .....	0.00	1.0301	0.000	1.0000	0.68410	0.99825
	25.00	1.3092	8.089	1.2709	0.86901	1.00250
	50.00	1.4921	16.179	1.4487	0.99040	1.00385
	100.00	1.7481	32.358	1.6970	1.1603	1.00742
	200.00	2.0873	64.717	2.0264	.....	1.01290
	400.00	2.4657	129.43	2.3937	.....	1.02422
	800.00	3.2487	258.8	3.1537	.....	1.046775
	1600.00	4.3114	517.7	4.1822	.....	1.09005
La(NO <sub>3</sub> ) <sub>3</sub> .2NH <sub>4</sub> NO <sub>3</sub> ....	3200.00	4.5657	1035.4	4.4322	.....	1.17243
	0.00	1.0301	0.000	1.0000	.....	0.99825
	26.34	0.9510	8.523	0.9231	.....	1.00112
	52.68	1.0156	17.046	0.9861	.....	1.00355
	105.36	1.1367	34.093	1.1034	.....	1.00971
	158.04	1.2303	57.14	1.1943	.....	1.01608
	196.83	1.3061	63.69	1.2679	.....	1.02183
	393.67	1.6016	127.38	1.5547	.....	1.04343
	787.35	2.0551	254.77	1.9950	.....	1.08286
	1574.70	2.8968	509.5	2.8120	.....	1.16652

We will now turn to a study of Fig. 5. The ordinates represent the fractional solubility of the dissolved salt, and the abscissas the fractional

concentration of the added salt. The heavy lines both solid and dotted represent the "theoretical limiting" curves for several types of salts. The coördinates for these curves were calculated by the following equations:

For a  $1,1 + 1$  or a  $2,2 + 2$  univalent salt with a univalent common ion added, or a bi-bivalent salt with a bivalent common ion added:

$$S(S + C) = 1.$$

For a  $1,2 + 1$  uni-bivalent salt with a univalent common ion added:

$$S(S + C)^2 = 1.$$

For a  $1,2 + 2$  uni-bivalent salt with a bivalent common ion added:

$$S^2(S + C) = 1.$$

For a  $1,3 + 1$  tri-univalent salt with a univalent common ion added:

$$S(S + C)^3 = 1.$$

For a  $1,3 + 3$  tri-univalent salt with a trivalent common ion added:

$$S^3(S + C) = 1.$$

For a  $1,4 + 1$  uni-tetravalent salt with a univalent common ion:

$$S(S + C)^4 = 1.$$

For a  $1,4 + 4$  uni-tetravalent salt with a tetravalent common ion:

$$S^4(S + C) = 1.$$

For a  $2,3 + 2$  bi-trivalent salt with a bivalent common ion:

$$S^2(S + C)^3 = 1.$$

For a  $2,3 + 3$  bi-trivalent salt with a trivalent common ion:

$$S^3(S + C)^2 = 1.$$

It was noted by Harkins, in the paper last referred to, that the curves of the salts of the  $1,1 + 1$  and the  $1,2 + 1$  types lie very close to the theoretical limiting curves, while the curves of the salts of the  $1,2 + 2$  type deviate from it very widely. Two experimental curves of salts of the

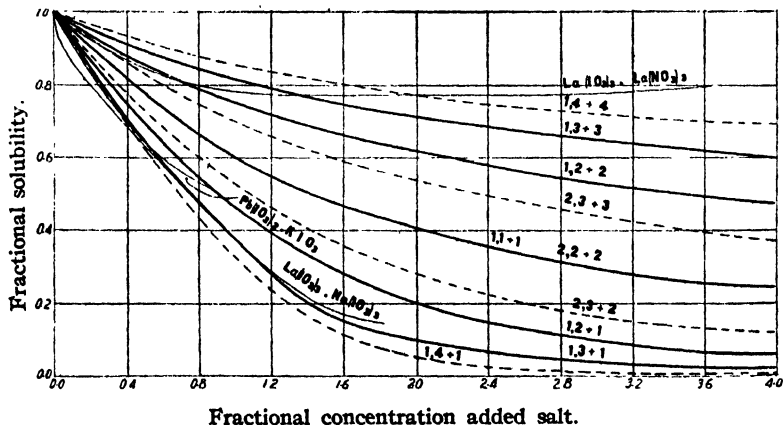


Fig. 3.—Theoretical limiting curves which express the fractional solubilities of various types of salts.

1,3 + 1, and the 1,3 + 3 types are interesting. In the first case the curve goes far below the theoretical limiting curve, then crosses and finally rises considerably above it, and in the second case we note a similar behavior, but the curve rises higher above the theoretical limiting curve. The latter part of this curve resembles the curves of the 1,2 + 3 type, and is similar to the curve showing the effect of the addition of a non-common ion. Harkins<sup>1</sup> found that several of the salts of the 2,1 + 1 type which he studied fell below the theoretical limiting curve. To see if a very insoluble salt of the 1,2 + 1 type would show this phenomenon to a greater degree, the curve for lead iodate in potassium iodate was plotted, and it may be seen that it falls about as far below as the curve for lanthanum iodate in potassium iodate and in general is similar in form. Of the two salts, lead iodate is much the more insoluble in water.

**6. Calculation of the Specific Conductance of Mixtures of Salts of the Tri-univalent Type.**—So far as is known to the writers no calculations have previously been made of the specific conductance of mixtures of salts of the tri-univalent type, at least not in cases where the salts in the mixture contain no common ion. For the calculations in this section the method employed is that previously used in the case of tri-ionic salts.<sup>2</sup> This method was first used to calculate the concentration of the constituents in mixtures of salts of the uni-univalent type, and has since been applied in a similar way for uni-bivalent salts. While from the standpoint of this paper, that is, that intermediate ions are present in solutions of salts of higher types, the calculated concentrations are only hypothetical, to those who still hold to the opposite theory they may appear to be real. In any event the results of such calculations will be of value for use in comparison of the uni-trivalent salts with those of lower types.

The values for the conductance and the conductance ratios of lanthanum nitrate and iodate, potassium and sodium iodates, and sodium nitrate, are given in Table IV, while Table V gives the apparent concentration of the constituents of mixtures in which lanthanum iodate is the saturating salt, and the added salts are lanthanum nitrate, potassium iodate and sodium nitrate. The logarithm of the apparent concentration of the un-ionized part of the saturating salt, lanthanum iodate (Table VI), is plotted against the logarithm of the apparent total ion concentration in Fig. 4, and Fig. 5 gives the similar values for the apparent solubility product, as calculated in Table VII. Tables VIII, IX and X give the similar values for a uni-bivalent salt, lead iodate.

When allowance is made for the fact that the concentration of a saturated lanthanum iodate solution is only about 0.001 molar, so that small errors in the conductance measurements produce a considerable per-

<sup>1</sup> THIS JOURNAL, 33, 1855 (1911).

<sup>2</sup> Harkins, *Loc. cit.*

TABLE IV.—CONDUCTANCE RATIO FOR SEVERAL SALTS.

Salt.	Conc. $\times 10^3$ .	Equivalent conductance		100r.	$Z_i \times 10^3$ .
		measured at 25°.	from work of others.		
La(IO <sub>3</sub> ) <sub>3</sub> .....	3.09	99.206	....	88.92	2.7479
La(NO <sub>3</sub> ) <sub>3</sub> .....	0.00	(142.6)	(142.6) <sup>1</sup>	100.00	0.0
	2.00	128.8	128.9	90.32	1.8065
	5.00	122.4	....	85.83	4.2917
	10.00	116.6	....	81.76	8.1768
	50.00	99.70	99.7	69.90	34.9533
	100.00	91.80	91.8	64.37	64.3780
	200.52	83.43	83.5	58.50	117.3135
KIO <sub>3</sub> .....	0.00	(114.37)	....	100.00	0.0
	0.20	113.00	....	98.80	0.1976
	0.50	112.37	....	98.25	0.49125
	1.00	111.57	....	97.55	0.97550
	2.00	....	....	96.50	1.930
	5.00	....	....	94.60	4.730
	10.00	....	....	92.80	9.280
	20.00	....	....	90.30	18.060
	50.00	....	....	86.0	43.000
	100.00	....	....	81.9	81.900
	200.00	....	....	77.5	155.000
NaIO <sub>3</sub> .....	0.00	....	....	100.00	0.0
	1.00	....	....	97.1	0.971
	2.00	....	....	96.0	1.920
	5.00	....	....	93.9	4.695
	10.00	....	....	91.7	9.170
	20.00	....	....	89.0	17.80
	50.00	....	....	84.2	42.10
	100.00	....	....	80.1	80.10
	200.00	....	....	75.2	150.40
NaNO <sub>3</sub> .....	0.00	(121.80)	....	100.00	0.0
	1.00	120.47	....	98.90	0.9890
	2.00	119.19	....	97.79	1.955
	10.00	114.00	....	93.58	9.358
	20.00	....	....	91.0	18.200
	50.00	....	....	87.1	43.550
	100.00	....	....	83.2	83.200
	200.00	....	....	78.8	157.600

centage effect, it will be seen that the calculated specific conductances of the mixtures are very closely in accord with the determined values, when either the common univalent ion is added, or when the added salt is sodium nitrate, which has no common ion. It is remarkable that an empirical equation of the general form of the Storch equation, derived entirely from the behavior of uni-univalent or the simplest type salts, can be used to calculate with as good an accuracy as this, the conductance of mixtures of salts of such a high type as the uni-trivalent. However,

<sup>1</sup> Cf. Noyes and Falk, THIS JOURNAL, 34, 454-485 (1912).

TABLE V.--APPARENT CONCENTRATION OF THE CONSTITUENTS OF SOLUTIONS SATURATED WITH LANTHANUM IODATE IN MILLIEQUIVALENTS PER LITER.

Salt added.	Conc. of salt.	Sol. La(IO <sub>3</sub> ) <sub>3</sub> .	Conc. un-ion. La(IO <sub>3</sub> ) <sub>3</sub> .	Conc. La <sup>+++</sup> .	Conc. 10 <sup>-1</sup> .	Zi.	Conc. uni-on. NaNO <sub>3</sub> .
La(NO <sub>3</sub> ) <sub>3</sub> ....	0.00	3.090	0.3424	2.748	2.748	2.748	.....
	2.00	2.529	0.336	3.918	2.193	3.918	.....
	5.00	2.391	0.379	6.197	2.011	6.197	.....
	10.00	2.348	0.455	9.911	1.890	9.911	.....
	50.00	2.496	0.761	36.498	1.739	36.498	.....
	100.00	2.809	1.003	65.981	1.805	65.981	.....
	200.52	3.359	1.391	119.217	1.967	119.215	.....
KIO <sub>3</sub> .....	0.0000	3.0900	0.3424	2.748	2.748	2.748	.....
	0.0990	2.8431	0.3050	2.538	2.633	2.633	.....
	0.2000	2.7300	0.2950	2.535	2.627	2.627	.....
	0.4957	2.5463	0.2803	2.266	2.741	2.741	.....
	0.5000	2.5400	0.2800	2.260	2.739	2.739	.....
	0.9914	2.2466	0.2561	1.990	2.939	2.939	.....
	1.0000	2.2400	0.2550	1.985	2.938	2.938	.....
	1.9828	1.6897	0.2037	1.486	3.400	3.400	.....
	3.9656	0.7898	0.1078	0.682	4.440	4.440	.....
NaNO <sub>3</sub> .....	0.00	3.0900	0.3424	2.748	2.748	2.748	.....
	1.00	3.1299	0.3020	2.720	2.720	3.685	0.0087
	2.00	3.169	0.2642	2.720	2.720	4.620	0.0330
	10.00	3.450	0.1663	2.720	2.720	11.940	0.5561
	25.00	3.928	0.1209	2.853	2.853	25.253	2.2810
	50.00	4.476	0.0940	3.020	3.020	46.320	6.1840
	100.00	5.244	0.0754	3.220	3.220	86.070	16.34
		Conc. un-ion. KIO <sub>3</sub> or NaIO <sub>3</sub> .	Conc. Na <sup>+</sup> or K <sup>+</sup> .	Conc. NO <sub>3</sub> <sup>-</sup> .	L × 10 <sup>1</sup> calc.	L × 10 <sup>1</sup> detd.	
La(NO <sub>3</sub> ) <sub>3</sub> ....	0.000	.....	.....	0.000	0.3066	0.3066	
	0.275	.....	.....	1.725	0.4906	0.4763	
	0.815	.....	.....	4.185	0.8212	0.7991	
	1.980	.....	.....	8.020	1.3546	1.3101	
	15.241	.....	.....	34.759	5.1505	5.1076	
	35.820	.....	.....	64.180	9.3520	9.2858	
	0.083270	.....	.....	117.250	16.9393	16.7520	
KIO <sub>3</sub> .....	.....	.....	.....	.....	0.3066	0.3066	
	.....	0.00408	0.0949	.....	0.2940	.....	
	.....	0.00820	0.1918	.....	0.2902	0.2803	
	.....	0.0208	0.4749	.....	0.3071	.....	
	.....	0.0210	0.4790	.....	0.3069	0.3024	
	.....	0.0429	0.9485	.....	0.3306	.....	
	.....	0.0430	0.9570	.....	.....	.....	
	.....	0.0918	1.891	.....	0.3830	.....	
	.....	0.2070	3.758	.....	0.5059	.....	
NaNO <sub>3</sub> .....	.....	.....	.....	.....	0.3066	0.3066	
	0.1093	0.0420	0.95	0.95	0.4192	0.4148	
	0.1879	0.0747	1.90	1.90	0.5349	0.5298	
	0.5700	0.2134	9.20	9.20	1.426	1.413	
	0.9539	0.3715	22.40	22.40	3.0466	.....	
	1.3607	0.5536	43.30	43.30	5.6108	.....	
	1.9472	0.7963	82.85	82.85	10.4500	.....	

TABLE VI.—CONCENTRATION OF THE UN-IONIZED PART OF LANTHANUM IODATE IN SOLUTIONS OF THE SALTS. (CONCENTRATIONS IN MILLIEQUIVALENTS PER LITER.)

Zi.	La(NO <sub>3</sub> ) <sub>3</sub>	KIO <sub>3</sub>	NaNO <sub>3</sub>
2.748	0.3424	0.3424	0.3424
2.633	....	0.3050	....
2.627	....	0.2950	....
2.739	....	0.2800	....
2.938	....	0.2550	....
3.400	....	0.2037	....
3.685	....	....	0.3020
3.918	0.3360	....	....
4.440	....	0.1078	....
4.620	....	....	0.2642
6.197	0.379	....	....
9.911	0.455	....	....
11.940	....	....	0.1663
25.253	....	....	0.1209
36.498	0.761	....	....
46.320	....	....	0.0940
65.981	1.003	....	....
86.070	....	....	0.0754
119.217	1.391	....	....

TABLE VII.—VALUES OF THE APPARENT SOLUBILITY PRODUCT FOR LANTHANUM IODATE IN THE PRESENCE OF OTHER SALTS.

(Zi in Milliequivalents, Solubility Product in Millimols.)

Zi.	La(NO <sub>3</sub> ) <sub>3</sub>	KIO <sub>3</sub>	NaNO <sub>3</sub>
2.748	19.0090	19.009	19.009
2.633	....	15.442	....
2.627	....	14.715	....
2.739	....	15.472	....
2.938	....	16.781	....
3.400	....	19.467	....
3.685	....	....	18.288
3.918	13.774	....	....
4.440	....	19.895	....
4.620	....	....	18.288
6.197	16.800	....	....
9.911	22.304	....	....
11.940	....	....	18.288
25.253	....	....	22.084
36.49	63.981	....	....
46.32	....	....	27.729
65.98	129.345	....	....
86.07	....	....	35.834
119.21	302.43	....	....



TABLE VIII.—CONCENTRATION OF THE CONSTITUENTS OF SOLUTIONS SATURATED WITH LEAD IODATE IN MILLIEQUIVALENTS PER LITER.

Salt added.	Conc. of salt.	Sol. $\text{Pb}(\text{IO}_3)_2$	Conc. un-ion. $\text{Pb}(\text{IO}_3)_2 \times 10^4$	Conc. $\text{Pb}^{++}$	Conc. $10^{-3}$	Zi.	Conc. un-ion. $\text{KNO}_3$
$\text{Pb}(\text{NO}_3)_2$ .....	0.00	0.1102	1.762	0.10844	0.10844	0.10844	....
	0.10	0.0870	1.850	0.18303	0.08515	0.18303	....
	1.00	0.0411	2.240	0.98400	0.03886	0.98450	....
	10.00	0.0185	2.870	8.4626	0.01563	8.4626	....
	100.00	0.0160	5.840	63.57	0.01016	63.51	....
$\text{KIO}_3$ .....	0.00000	0.1102	1.762	0.10844	0.10844	0.10844	....
	0.05304	0.0697	1.180	0.06852	0.12104	0.12104	....
	0.10610	0.0437	0.800	0.04290	0.14791	0.14791	....
$\text{KNO}_3$ .....	0.00	0.1102	1.762	0.10844	0.10844	0.108	0.0000
	2.00	0.1141	0.463	0.10510	0.10510	2.044	0.0570
	10.00	0.1334	0.256	0.11150	0.11150	9.482	0.6114
	50.00	0.2037	0.208	0.14000	0.14000	43.490	6.6500
Salt added.	Conc. un-ion. $\text{Pb}(\text{NO}_3)_2$	Conc. $\text{KIO}_3$	Conc. $\text{K}^+$	Conc. $\text{NO}_3^-$			
$\text{Pb}(\text{NO}_3)_2$ .....	0.00000	.....	.....	.....			
	0.00212	.....	.....	.....			
	0.0546	.....	.....	.....			
	1.553	.....	.....	.....			
	36.500	.....	.....	.....			
$\text{KIO}_3$ .....	.....	0.00000	0.00000	.....			
	.....	0.00052	0.05252	.....			
	.....	0.00105	0.10505	.....			
$\text{KNO}_3$ .....	.....	.....	0.000	0.000			
	.....	.....	1.939	1.939			
	.....	.....	9.370	9.370			
	.....	.....	43.350	43.350			
	.....	.....	.....	.....			

TABLE IX.—VALUES FOR THE SOLUBILITY PRODUCT FOR LEAD IODATE IN THE PRESENCE OF OTHER SALTS. (Zi IN MILLIEQUIVALENTS, SOLUBILITY PRODUCT IN MILLIMOLS.)

Zi.	$\text{Pb}(\text{NO}_3)_2$	$\text{KIO}_3$	$\text{KNO}_3$
0.10844	0.0006376	0.0006376	0.0006376
0.12104	.....	0.0005087	.....
0.14791	.....	0.0004693	.....
0.18303	0.00066351	.....	.....
0.98400	0.0007430	.....	.....
2.044	.....	.....	0.0005810
8.4626	0.0010337	.....	.....
9.482	.....	.....	0.0006931
43.490	.....	.....	0.001372
63.500	0.0032783	.....	.....

TABLE X.—CONCENTRATION OF THE UN-IONIZED PART OF LEAD IODATE IN SOLUTIONS OF OTHER SALTS. (CONC. IN MILLIEQUIVALENTS PER LITER.)

$\Sigma i$	$Pb(NO_3)_2$	$KIO_3$	$KNO_3$
0.10844	0.001762	0.001762	0.001762
0.12104	....	0.001180	....
0.14791	....	0.000800	....
0.18303	0.001850	....	....
0.98400	0.002240	....	....
2.044	....	....	0.000463
8.463	0.002870	....	....
9.482	....	....	0.000256
43.490	....	....	0.000208
63.510	0.005840	....	....

when the common ion is trivalent the agreement is not nearly so good, and the calculated values becomes several per cent. higher than that determined by experiment. This is in the direction of the change of conductivity which occurs when there is a small amount of complex formation.

Fig. 4 shows the variation in the apparent total ion concentration

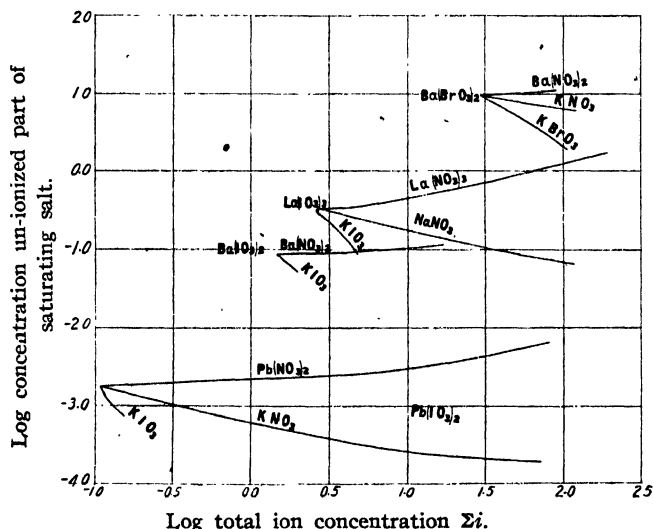


Fig. 4.—The solubility of the un-ionized part of the salts calculated on the assumption that intermediate ions are not present.

for three uni-bivalent salts, lead iodate, barium iodate and barium bromate, and for one uni-trivalent salt, lanthanum iodate. Raising and shifting the curve for barium iodate toward one side will show how closely parallel are the similar curves for barium bromate and iodate, even although the former salt is 25 times as soluble as the latter. Lead chloride is about seven hundred times as soluble as lead iodate, yet a

comparison of the sets of curves for the two salts shows that the similar curves still remain very nearly parallel. It is remarkable that when a uni-univalent salt with a *non-common ion* is added, the curve for the apparent concentration of the un-ionized part of the saturating salt has practically the same slope whether the saturating salt is uni-, bi-, or tri-univalent.

In the case of the uni-univalent salt the apparent solubility of the un-ionized part always falls, at practically the same rate with the total ion concentration, no matter what the type of the added salt may be. However, in the case of the uni-bivalent salts the solubility of the apparent un-ionized part decreases much more rapidly when the common univalent ion is added, and what is much more remarkable, increases when the common ion is bivalent. We now find exactly the same result for the uni-trivalent salt, but in this case the apparent solubility of the un-ionized part increases much more rapidly at the same total ion concentration, than it does in the case of the uni-bivalent salts barium iodate and barium bromate, which are the most nearly similar in solubility. It may thus be said that these effects which are abnormal in the case of the uni-bivalent salts, become even more abnormal with this tri-univalent salt.

It is thus seen that when the concentration of the constituents of a mixture is calculated by the ordinary method, that in the case of higher type salts, the non-common ion salts have a seemingly normal effect upon the solubility of the non-ionized part of the salt, but that when a common univalent ion is added the effect is abnormal in giving an extraordinary depression in solubility, while with the common bivalent ion there is the much more abnormal and even absurd result that the solubility of the un-ionized part of the salt seems to rise rapidly. It has been shown by Harkins<sup>1</sup> that when calculations are made upon the basis of the non-existence of intermediate ions, just such abnormal results should be obtained in case intermediate ions are present, and that, if allowance is made for the presence of intermediate ions, according to the calculations presented in Table I of the present paper, these irregularities disappear, as well as the irregularities found in the behavior of the solubility product, as shown in Fig. 5. Thus assuming that Table I gives the proper percentage ionization of salts of the uni-bivalent type, it is found that upon calculation that the true solubility of the un-ionized part decreases at nearly the same rate, with the total ion concentration, no matter whether the salt added contains no common ion, a common univalent, or a common bivalent ion. That the somewhat greater abnormalities in the case of the tri-univalent salt could be as readily smoothed away seems certain

<sup>1</sup> *Loc. cit.*

when it is remembered that in the solution of such a salt there would be two intermediate ions instead of one.

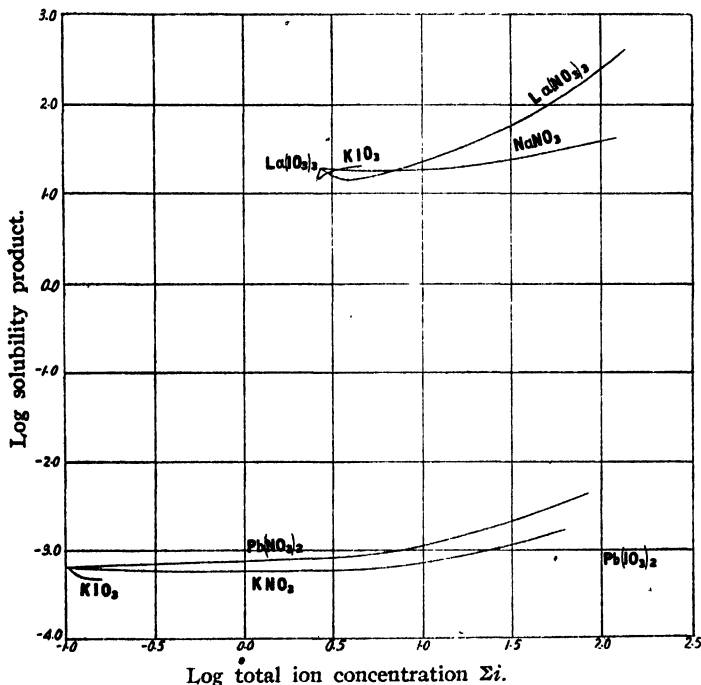


Fig. 5.—The solubility product calculated on the assumption that intermediate ions are not present.

**7. Summary of Experimental Part.**—1. Equations are given for the calculation of the constituents of mixtures of salt solutions both on the basis of the non-existence and existence of intermediate ions. A comparison of the degrees of ionization of several substances calculated on both assumptions is also made.

2. Pure lanthanum iodate was made and its solubility at  $25^\circ$  was determined in solutions of salts containing common univalent ions, common trivalent ions, and non-common ions. It was found that: (a) the solubility decreases rapidly as the concentration of the salt having a common univalent ion increases; (b) the solubility decreases slightly at first and then increases as a salt with a common trivalent ion is added, the curve approaching the curve for the non-common ion effect.

3. Conductance measurements were made on the dilute solutions.

4. Calculations of the constituents of the mixtures of the solutions were made and curves were drawn to show the changes in the solubility products and concentrations of the un-ionized part with changes in the total ion concentration. In these calculations, intermediate ions are

assumed to not exist. It was found that the apparent concentration of the *un-ionized part* is affected normally by the addition of non-common ion salts; is affected abnormally by the presence of salts having a common univalent ion in that it gives an extraordinary depression; is affected even more abnormally by the addition of salts having a common trivalent ion, giving a rapid rise in the apparent solubility. These abnormalities disappear if intermediate ions are assumed to be present.

5. The theoretical discussion has not been summarized, since it has been given in a condensed form in the body of the paper.

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

## THE EFFECT OF SALTS UPON THE SOLUBILITY OF OTHER SALTS. VIIIa. THE SOLUBILITY RELATIONS OF A VERY SOLUBLE BI-UNIVALENT SALT.

BY WILLIAM D. HARKINS AND HARRY M. PAINE.

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### Introduction.

Since, as has been shown in previous papers of this series,<sup>1</sup> the moderately soluble uni-bivalent salts show such a wide variation from the solubility product principle, an investigation of the effect of the addition of salts to a bi-univalent salt of extremely high solubility was considered advisable. Strontium chloride with a solubility at 25° of 7.034 equivalents per 1000 grams of water, seemed to be the salt best suited for this purpose. Its solubility at 25° was determined in water and in various concentrations of strontium nitrate, sodium nitrate, nitric acid, hydrochloric acid, hydrobromic acid, hydriodic acid, potassium iodide, potassium chloride, cupric chloride, and potassium nitrate. The densities of all solutions and mixtures were measured. In calculations the atomic weights for 1911 were used and all weighings reduced to vacuum.

### Preparation of Salts.

**Strontium Chloride.**—A special grade of strontium chloride was recrystallized from conductivity water and the salt preserved in a moist condition in closely stoppered bottles.

**Sodium Nitrate.**—Sodium nitrate was recrystallized twice from conductivity water.

**Hydrochloric and Nitric Acids.**—"C. P." acids were used after careful testing.

**Hydriodic Acid.**—This acid was prepared by careful hydrolysis of phosphorus triiodide, with exclusion of air. The product obtained was carefully redistilled and showed no test for free iodine.

**Hydrobromic Acid.**—The acid was prepared in a manner analogous to that used for hydriodic acid.

<sup>1</sup> THIS JOURNAL, 33, 1808 (1911).

**Potassium Chloride.**—Potassium chloride "Zur analyse" was recrystallized twice from conductivity water.

**Potassium Iodide.**—The best potassium iodide obtainable was recrystallized from conductivity water.

**Cupric Chloride.**—This salt was recrystallized twice from conductivity water.

**Potassium Nitrate.**—Potassium nitrate was recrystallized three times from conductivity water.

### Methods of Analysis.

**Chloride, Bromide or Iodide.**—The halogens were determined by adding to the solutions, containing these radicals, a little less than an equivalent amount of dilute silver nitrate solution, allowing to stand overnight, and adding a slight excess of silver nitrate the next day.<sup>1</sup> The precipitates were transferred to platinum Gooch crucibles and washed with very dilute silver nitrate solution and then with water containing a little nitric acid. The weight of the precipitate weighed was about 2 g.

**Acids.**—These were determined by titration with 0.1 *N* sodium hydroxide which had been previously standardized against hydrochloric acid, the strength of which was determined gravimetrically.

**Nitrates.**—Several methods were thoroughly tried out and in every case where the nitrogen was finally obtained as ammonia, from strongly alkaline solution, it was found that the gelatinous strontium hydroxide precipitate adsorbed the nitrate sufficiently to destroy the accuracy of the result. The Pelouze-Fresenius method which depends on the oxidation of ferrous iron in a solution strongly acidified with hydrochloric acid was used. This was done in an atmosphere of carbon dioxide, carefully freed from oxygen, obtained from a Kipp generator charged with marble previously boiled in conductivity water, and hydrochloric acid boiled for fifteen minutes just previous to use. Cuprous chloride was added to absorb any remaining oxygen and a layer of oil poured over the acid on the surface exposed to air.

The carbon dioxide produced was further purified by passing through a tower of chromous acetate and then through conductivity water. A weighed amount of pure iron was dissolved in hydrochloric acid and the nitrate solution run in through a dropping funnel, care being taken to prevent the entrance of air. After standing for fifteen minutes at 100° the compound resulting from the addition of nitric oxide to the ferrous chloride was broken up by boiling, the solutions cooled, and in duplicate experiments titrations were made with both potassium permanganate and potassium dichromate. Carefully carried out this method gave, with solutions of known concentration, results always within 0.1% of the amount taken.

**Strontium.**—When required the strontium was determined by precipitation as carbonate and weighing both as carbonate and sulfate.

**Copper.**—This was determined by the iodide method using the modification suggested by Lowe.<sup>2</sup> In this as in all other volumetric methods employed, weight burets were used, and weighed amounts of solutions were taken.

**Iodides.**—In the determination of strontium chloride in potassium iodide a total halogen analysis was made and the iodine determined in a fresh portion of solution by the method of Bray and MacKay.<sup>3</sup>

### Solubility Measurements.

The results of the solubility determinations are given in Table I. In the majority of cases each point was checked by four duplicates.

<sup>1</sup> Richards, "Researches Concerning Atomic Weights," *Carnegie Publication*, p. 17 (1907).

<sup>2</sup> "Technical Methods of Ore Analysis," p. 77.

<sup>3</sup> THIS JOURNAL, 32, 1193-1204 (1910).

TABLE I.—SOLUBILITY OF STRONTIUM CHLORIDE IN SALT SOLUTIONS AT 25°.

Salt added.	Equiv. of added salt in 1000 g. H <sub>2</sub> O.	Sol. per 1000 g. soln.	Sol. per 1000 g. H <sub>2</sub> O.	Sol. equiv. per 1000 g. H <sub>2</sub> O.	Density 25°/4°.
None	None	358.0	557.6	7.034	1.4015
Sr(NO <sub>3</sub> ) <sub>2</sub> .....	0.1372	354.2	558.5	7.044	1.4113
	0.5766	344.7	558.0	7.038	1.4336
	1.0988	333.0	557.2	7.030	1.4636
	3.318	289.7	551.4	6.956	1.6664
Solid Sr(NO <sub>3</sub> ) <sub>2</sub>					
NaNO <sub>3</sub> .....	0.3621	356.3	570.6	7.198	1.4216
	0.5010	356.0	576.4	7.270	1.4588
	3.553	308.8	584.8	7.276	1.5214
	6.856	255.3	542.6	6.844	1.5581
Solid Sr(NO <sub>3</sub> ) <sub>2</sub>					
HNO <sub>3</sub> .....	0.1771	355.2	557.0	7.028	1.4038
	0.3521	354.0	557.6	7.034	1.4059
	1.277	340.4	557.6	7.034	1.4175
HCl.....	0.1551	351.7	545.6	6.882	1.3953
	0.5162	336.0	515.5	6.502	1.3788
	1.017	314.2	475.2	5.996	1.3563
	2.165	263.3	385.6	4.864	1.3065
	9.205	30.55	42.09	0.530	1.1498
HBr.....	0.06817	354.7	552.8	6.974	1.4020
	0.4191	339.2	530.7	6.696	1.4010
	0.9716	315.2	496.5	6.262	1.3992
	1.154	207.8	486.2	6.132	1.3995
HI.....	0.1641	348.5	546.2	6.890	1.4058
	0.4462	332.8	527.3	6.650	1.4121
	0.4126	334.8	529.1	6.672	1.4119
	0.7539	315.2	504.6	6.366	1.4196
KI.....	0.09199	354.5	557.6	7.034	1.4093
	0.5401	337.9	556.2	7.016	1.4466
	0.6015	336.0	558.0	7.038	1.4513
	1.445	309.0	554.4	6.992	1.5154
KCl.....	0.0719	356.2	556.2	7.016	1.4032
	0.433	348.0	550.9	6.950	1.4085
	0.8576	338.9	545.5	6.882	1.4152
	1.594	324.0	536.2	6.764	1.4266
CuCl <sub>2</sub> .....	0.7134	340.05	540.0	6.812	1.4200
	2.276	304.0	503.6	6.352	1.4595
KNO <sub>3</sub> .....	0.09796	358.6	564.6	7.122	1.4107
	0.4755	359.0	587.0	7.406	1.4349

The principal object of this investigation was to show that the predictions based upon the earlier investigations on the less soluble salts of the uni-bivalent type is true, namely, that the form of the solubility curve for the addition of a salt with a common bivalent ion is, on the whole, the same as that for the addition of a salt with no common ion when the

saturating salt is a very soluble one.<sup>1</sup> The first step in the ionization of strontium chloride is



and in a very concentrated solution this should be almost the only form of ionization. However, the second step in the ionization



must take place to a slight extent, and for this reason in solutions of strontium chloride and nitrate there should be a small percentage of the common  $\text{Sr}^{++}$  ion. Since the ions present to the greatest extent are the non-common  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SrCl}^+$ , and  $\text{SrNO}_3^+$  ions, the curve should have the same form as for the addition of a salt with no common ion, but might fall slightly below the non-common ion curve on account of the presence of the small percentage of the common  $\text{Sr}^{++}$  ion.

That this is true is shown by the data in Table I. Thus the solubility of strontium chloride in solutions of strontium nitrate is practically the same as in water itself, and this is true also for nitric acid. Here the curves representing the effect of the common bivalent ion, and of no common ion, are the same. If, however, sodium nitrate is added the solubility of the strontium chloride increases slightly up to a concentration of 3.5 equivalents of sodium nitrate, but this increase amounts to only 5%. When the non-common ion salt potassium iodide is added, the solubility of the strontium chloride remains constant, just as when nitric acid or strontium nitrate is added. It is therefore found that in saturated solutions the solubility relationships seem, in so far as they bear upon the question at all, to accord with the hypothesis of intermediate ion formation, though the specific solubility effects are so great in these extremely concentrated solutions that this fact cannot be considered as bearing very strongly upon this question.

The principal work upon the effects of salts on the solubility of extremely soluble salts was done by Engel,<sup>2</sup> who developed the empirical rule that the addition of an acid to the saturated solution of an extremely soluble salt precipitates an equivalent quantity of the salt, and Armstrong<sup>3</sup> and others suppose that the reduction of solubility caused by an acid, or by a salt, is caused by the appropriation of solvent molecules by the substance which is introduced. According to the idea of Armstrong, strontium nitrate, potassium iodide and nitric acid do not appropriate any of the solvent.

The data given in Table I show that the solubility of strontium chloride

<sup>1</sup> However it was realized that in the case of so soluble a salt as strontium chloride, what may be called specific solubility, might largely, but probably not entirely, mask this result.

<sup>2</sup> *Compt. rend.*, 102, 619 (1886); 104, 433 (1887); *Ann. chim. phys.*, [6] 13, 376 (1888).

<sup>3</sup> *Proc. Roy. Soc.*, (A) 79, 564; 84, 123.



is greatly decreased by the addition of any halogen acid, whether or not the acid contains a common ion, but the solubility is not very greatly depressed by the addition of any of the alkali salts of the halogens which were used. While the salting out effect of the common chlorine ion is marked, it is plain that what may be called specific effects have become very prominent in these extremely concentrated solutions. This may be considered as probably due to a real solubility effect, and it seems that solutions of the halogen acids are poor solvents for salts, at least for the salts of the alkalis and alkaline earths.

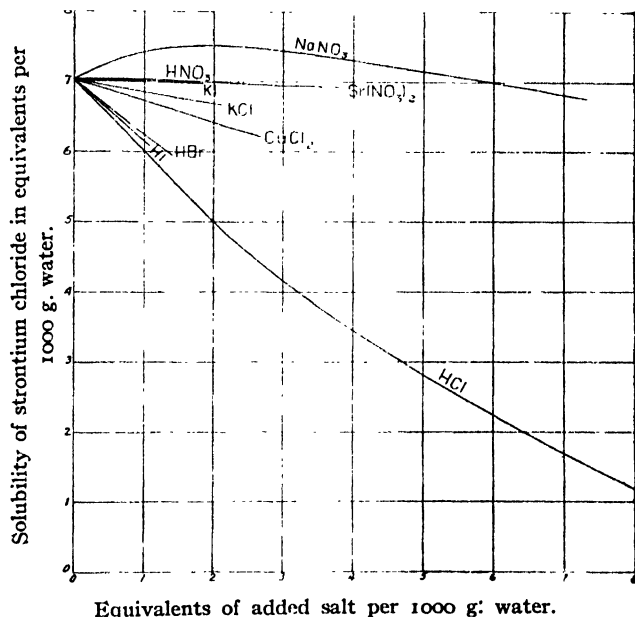


Fig. 1.—Solubility of strontium chloride in equivalents per 1000 g. water at 25° C.

Fig. 1 shows that of the non-common ion acids, hydrobromic and hydriodic very greatly depress the solubility of strontium chloride, while in nitric acid the solubility per 1000 g. of water is the same as in the water alone. Since the curve for hydrobromic lies above that for hydriodic acid, it may be assumed that the hydrochloric acid curve would lie higher still were it not for its common ion effect. Just as hydrochloric acid depresses the solubility more than hydrobromic acid, so potassium chloride gives this effect more strongly than potassium iodide. The curves for sodium nitrate and nitric acid have, on the whole, the same relative positions as those for potassium iodide and hydriodic acid, and for potassium chloride and hydrochloric acid. In all of these cases the strontium chloride is much less soluble in the acid than in the corresponding salt solution. From the literature of the subject we would judge

that the salts of the alkalis are less soluble in solutions of bases, than in the corresponding salt solutions. Cupric chloride depresses the solubility much more than potassium chloride. The curve for the non-common ion effect of potassium nitrate is not plotted in the figure, but it lies close to the sodium nitrate curve, and only slightly above it. It was shown in an earlier paper that solubility effects, in general, can be divided into four classes. The specifically great depressing action of the acids upon very soluble salts gives a fifth class which is important.

Other specific effects have been noticed in work upon very soluble salts. For example, other salts seem in general to show a specially high solubility when the added salt is a nitrate. Thus a chloride depresses the solubility of a nitrate much more than the nitrate depresses the solubility of the chloride.

The fact that solutions of the halogen acids are much poorer solvents for salts of the alkalis and alkaline earths is important in connection with the determination of the relative degrees of ionization of these acids and salts. From conductivity measurements alone it was at one time supposed that hydrogen chloride is more highly ionized in aqueous solution than is potassium chloride. However, a study of the change of the migration values of the ions with the concentration has led to the idea that it is quite probable that the acid is not more highly ionized. The evidence obtained from solubility measurements has been opposed to the idea that both have the same ionization, since in dilute saturated solutions the solubility of a chloride is more depressed by hydrochloric acid than by an equivalent amount of potassium chloride. Now that it has been shown that hydrochloric acid is a poorer solvent for salts than a solution of potassium chloride, it destroys the supposed value of the evidence obtained by solubility measurements; or, since in dilute solutions the difference between the salting out effects of the acid and the salt is very small, it may be considered that if anything the solubility results tend to help prove that potassium chloride and hydrochloric acid are dissociated to practically the same extent.

CHICAGO, ILL.

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

## THE EFFECT OF SALTS UPON THE SOLUBILITY OF OTHER SALTS. VIII<sup>b</sup>. THE SOLUBILITY RELATIONS OF SOME EXTREMELY SOLUBLE SALTS.

By WILLIAM D. HARKINS AND W. TUDOR PEARCE.

Received August 18, 1916.

### Introduction.

In the preceding paper the solubility relations of the very soluble uni-bivalent salt, strontium chloride, have been discussed, and the present

paper will extend the work to three other salts, strontium bromide, which is extremely soluble (8.6 equivalents to 1000 g. of water), and to two pentaionic salts, potassium and sodium ferrocyanides. Extremely variable results have heretofore been obtained upon the solubility of potassium ferrocyanide in water. Thus the results vary from 28 to 48 g. per 100 g. of water at 25°. The data obtained by us give this value as 24.796 g. per 100 g. of water.

The principal object of this paper was to see if with these extremely soluble salts the effect of the presence of intermediate ions upon the solubility relations could be found, after allowances are made for the specific effects which are extremely large in solutions of such high concentration. The effect to be expected, if intermediate ions are present, is that the solubility should not be depressed by the addition of a salt with a common ion of a valence of more than one, and that the increase of solubility should increase with the valence of the common ion. That this is just what is found experimentally may be seen, but it is difficult to determine how much of the effect is due to the presence of intermediate ions, since there is no exact method for determining the magnitude of what have been called the specific solubility effects. However, the results of the work presented in these two papers, when compared with the data collected in the literature on lower type salts, seem to indicate that a part of this effect must be due to intermediate ions.

### Experimental.

**Preparation of Solutions.**—Salts of the highest purity obtainable commercially were crystallized from conductivity water in all cases and the method of procedure was the same as the one referred to in the preceding paper.

**The Solubility of Strontium Bromide in Strontium Nitrate.**—The bromine was determined by weighing as silver bromide. The precipitant, 0.01 *N* silver nitrate, was added in very slight excess. The precipitate was washed with 0.01 *N* nitric acid and finally with water very slightly acid. It was weighed in a Gooch crucible.

The nitrogen was determined by the Kjeldahl-Gunning-Jodwohl method with the usual precautions, *viz.*, letting the digestion mixture stand overnight and when distilling to continue the process until the flask is nearly dry. The results in grams per 1000 g. of water are given in Table I and shown graphically in Fig. 1.

**The Solubility of Potassium Ferrocyanide and Sodium Ferrocyanide in Each Other.**—The determination of hydroferrocyanic acid was made by a modification of de Haen's method. It was found necessary to use a very dilute solution and titrate in a definite time. To about 1 g. of ferrocyanide 100 cc. solution and 10 cc. of 0.5 *N* sulfuric acid were added and three minutes' time was taken for the titration.

The determination of potassium and sodium<sup>1</sup> were made by modification of the method given in Lunge's "Technical Analysis."<sup>2</sup> In order to get a satisfactory decomposition when the concentration of the added salt was high the following procedure was necessary: About 1 g. was taken for analysis. This was transferred to a beaker and diluted with 50 cc. of water; then 5 drops of sulfuric acid (1 : 10) were added, and

<sup>1</sup> Cf. Treadwell-Hall, Vol. II, p. 497.

<sup>2</sup> *Ibid.*, p. 729, Part 1; and *Ber.*, 36, 1930 (1903).

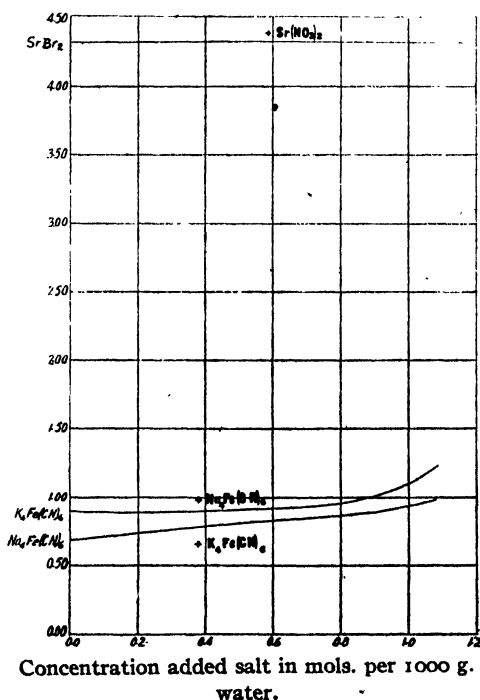
30 cc. of a filtered 0.1 *N* solution of ammonium persulfate. The solution was then warmed on water bath until colorless. If it was as still blue after forty minutes, another 30 cc. of ammonium persulfate were added. From this point on the method referred to gave satisfactory results.

To prevent oxidation, pure hydrogen was used to saturate all solutions before rotation and the air in the bottles was replaced by it. In spite of this precaution, decomposition certainly took place in some cases, as was made evident by the formation of a blue precipitate. In no case, except when the two solid phases were present, was a solution that gave a blue color to the asbestos mat through which it was filtered, used for analysis. In the exception mentioned, the solution analyzed showed only a faint coloration. All titrations were made and the samples for the potassium and sodium determinations taken, as quickly as was possible. However, it was noted that in all the solutions a blue precipitate was formed on standing, the amount of which increased with the time and with the concentration of the hydroferrocyanic acid. Although the change was very slight, and the agreement of duplicate analyses was good, so that the results when plotted give a fairly smooth curve, the degree of accuracy is not so great as was obtained in the work on the other salts.

### Solubility Measurements.

The results of the solubility measurements are given in Tables II and III and are shown graphically in Fig. 1.

Fig. 1 shows the interesting result, which is very similar to that obtained for strontium chloride,



that, up to 2.8 equivalent weight concentration (per 1000 g. of water) of added salt, the addition of strontium nitrate has no effect upon the solubility, that is, the solubility is expressed by a straight horizontal line. This is remarkable when it is considered that the most concentrated solution is 11.4 *N* with respect to total salt concentration. The data indicate that the solubility does not remain exactly constant, but the variation is extremely slight, only 0.78% for this wide range of concentrations.

The solubility results for potassium and sodium ferrocyanides are of even more interest, since they indicate that in the case of these salts of high type each salt increases the solubility of the other.

Fig. 1.—Solubility of some very soluble salts in solutions of other salts.

TABLE I.—SOLUBILITY OF STRONTIUM BROMIDE IN STRONTIUM NITRATE AT 25°. Concentration in mols. per 1000 g. H<sub>2</sub>O.

No.	Conc. Sr(NO <sub>3</sub> ) <sub>2</sub> .	Solubility Sr Br <sub>2</sub> .	Mean solubility.	Solubility grams per 1000 H <sub>2</sub> O.	Density 25°/4°.	Fractional conc of added salt.	Fractional solubility.
1.....	0.0000	4.3081s	.....	.....	.....	.....	.....
2.....	.....	4.3080	.....	.....	.....	.....	.....
3.....	.....	4.3079	.....	.....	.....	.....	.....
4.....	.....	4.3081s	4.3080s	1066.10	1.7002	0.0000	1.0000
5.....	0.0360	4.3105	.....	.....	.....	.....	.....
6.....	.....	4.3105s	4.3105	1066.95	.....	0.008356	1.0006
7.....	0.07216	4.3125s	.....	.....	.....	.....	.....
8.....	.....	4.31249	4.3125	1067.42	1.70325	0.016750	1.0010
9.....	0.14568	4.31702s	.....	.....	.....	.....	.....
10.....	.....	4.31697	4.3170	1068.54	1.72844	0.033815	1.0021
	0.30663	.....	.....	.....	.....	.....	.....
	.....	.....	4.3180	1068.80	1.73766	0.071173	1.0023
	0.61124	.....	4.3190	1069.17	1.74866	0.14188	1.0025
	1.8610	.....	4.3390	1073.97	1.77368	0.43199	1.0072

TABLE II.—SOLUBILITY OF POTASSIUM FERROCYANIDE IN SODIUM FERROCYANIDE AT 25°.

Concentrations in mols. per 1000 g. H<sub>2</sub>O.

Conc. Na <sub>2</sub> Fe(CN) <sub>6</sub> .	Solubility K <sub>4</sub> Fe(CN) <sub>6</sub> av. of sev'l anal.	Solubility in grams per 1000 g. H <sub>2</sub> O.	Density 25°/4°.
0.00000	0.894585	247.96	1.09081
0.05072	0.882720	.....	1.09900
0.06633	0.88544	.....	1.10039
0.12306	0.88088	.....	1.09350
0.25972	0.89116	.....	1.12796
0.4900	0.91600	.....	1.17241
0.87034	0.99000	.....	1.19700
0.91060	1.01200	.....	1.21190
0.95879	1.05177	.....	1.22673
1.04380	1.11590	.....	1.25789

TABLE III.—SOLUBILITY OF SODIUM FERROCYANIDE IN POTASSIUM FERROCYANIDE AT 25°.

Concentrations in mols. per 1000 g. H<sub>2</sub>O

Conc. K <sub>4</sub> Fe(CN) <sub>6</sub> .	Solubility Na <sub>4</sub> Fe(CN) <sub>6</sub> av. of sev'l anal.	Solubility g. per 1000 g. H <sub>2</sub> O.	Density 25°/4°.
0.0000	0.6818	207.25	1.0595
0.1327	0.7056	214.47	1.0199
0.1624	0.7117	216.30	1.0768
0.1789	0.7213	219.23	1.0792
0.2115	0.7253	220.44	1.1006
0.2722	0.7610	231.29	1.1113
0.3532	0.7814	237.49	1.1243
0.5850	0.8652	262.97	1.1567
0.6111	0.8712	264.79	1.1581
0.6994	0.8984	273.05	1.1830
1.0578	0.9588	291.40	1.2267

## Summary of Papers on Extremely Soluble Salts.

1. This paper and the one which precedes it give data for the solubility of the higher type salts, strontium chloride, strontium bromide, potassium ferrocyanide and sodium ferrocyanide, in solutions of different salts and acids. In these extremely concentrated solutions what may be called specific effects have become very prominent, so that the behavior of these salts does not give very definite evidence for or against the hypothesis of intermediate ion formation, but, nevertheless, the general solubility relations seem to be what would be expected if intermediate ions are present.

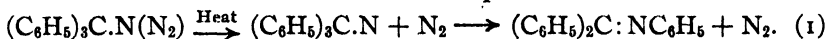
[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

## THE MOLECULAR REARRANGEMENT OF TRIARYLMETHYL-AZIDES.<sup>1</sup>

By JAMES KUHN SENIOR.<sup>2</sup>

Received September 21, 1916.

Molecular rearrangements have been observed by Stieglitz and his collaborators in the triphenylmethane series when triphenylmethyl hydroxylamines<sup>3</sup>  $\text{Ar}_3\text{C.NHOH}$  are subjected to the action of phosphorus pentachloride, and when triphenylmethylhalogenamines<sup>4</sup>  $\text{Ar}_3\text{C.NH(Hal)}$  are treated with alkaline reagents. These rearrangements are entirely analogous,<sup>5</sup> respectively, to the Lossen-Beckmann rearrangements of acyl hydroxylamines and ketoximes and the Hofmann rearrangement of acyl halogenamines  $\text{RCO.NH(Hal)}$ —in fact the rearrangements in the triphenylmethane series were anticipated and explored as the result<sup>6</sup> of the investigations of Stieglitz on the nature of the Lossen-Beckmann-Hofmann rearrangements. There is a third group of acyl derivatives, the azides  $\text{RCO.N}_3$ , which, as Curtius found, undergo exactly the same kind of rearrangement as do the acyl hydroxylamines and halogenamines. This parallelism, together with Stieglitz's theory that the rearrangement in all of these cases is due to the primary formation of univalent nitrogen<sup>7</sup> derivatives,  $\text{RCO.N}$ ,  $\text{R}_3\text{C.N}$ , etc., made it appear certain that triphenylmethylazides  $(\text{C}_6\text{H}_5)_3\text{C.N}_3$ , would be found, on investigation, to undergo a rearrangement analogous to that of triphenylmethyl hydroxylamines and halogenamines. Further, it was anticipated that for the rearrangement of the azides heat<sup>8</sup> alone would be required



With the object of determining these relations, I undertook, at the

<sup>1</sup> A brief preliminary report by Stieglitz and Senior appeared in the *Proc. Nat. Acad. of Sciences*, **1**, 207 (1915).

<sup>2</sup> The work presented in this paper forms, in part, the basis of a dissertation presented to the University of Chicago in partial fulfilment of the requirements for the Ph.D. degree.

<sup>3</sup> Stieglitz, Reddick and Leech, *Eighth Intern. Congr. Appl. Chem.*, **25**, 44 (1912); Stieglitz and Leech, *Ber.*, **46**, 2147 (1913); and *THIS JOURNAL*, **36**, 272 (1914).

<sup>4</sup> Stieglitz and Vosburgh, *Ber.*, **46**, 2151 (1913); Vosburgh, *THIS JOURNAL*, **38**, 2081 (1916).

<sup>5</sup> The literature references are given by Stieglitz and Leech, *THIS JOURNAL*, **36**, 272 (1914), and Stieglitz and Stagner, *Ibid.*, **38**, 2046 (1916).

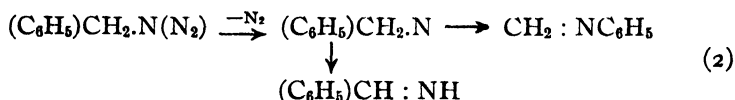
<sup>6</sup> Cf. *Ber.*, **46**, 2147 (1913).

<sup>7</sup> For the electronic formulation of the theory, see Stieglitz and Leech, *Loc. cit.*, and L. W. Jones, *Am. Chem. J.*, **50**, 440 (1913) (published in 1914); for preliminary suggestions, see Stieglitz, *Ber.*, **43**, 782 (1910); *THIS JOURNAL*, **36**, 276, 280, 288; and Jones, *Loc. cit.*, and *Am. Chem. J.*, **48**, 1 (1912).

<sup>8</sup> Stieglitz, *Am. Chem. J.*, **18**, 751 (1896); **29**, 49 (1903).

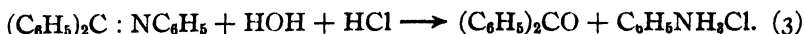
suggestion of Professor Stieglitz, the investigation of triphenylmethyl azide. This seemed particularly desirable because, for the azides, the alternative theory of a direct exchange<sup>1</sup> of radicals in these rearrangements seems quite inapplicable. Cumulative evidence that in every instance the azides behave exactly as do the hydroxylamines and the halogenamines was anticipated.

A rearrangement somewhat analogous to the one I proposed to investigate had already been observed by Curtius<sup>2</sup> in the case of benzyl azide, and Curtius also interprets the formation of the main products of the rearrangement by assuming the formation of a univalent nitrogen derivative:



The reagent used was not heat alone, but a strong acid and heat, and the reactions were complicated by subsequent changes of the main products.

On the other hand, triphenylmethylazide itself had been prepared by Wieland<sup>3</sup> in 1909 and found to be remarkably stable for an azide, differing markedly in this respect from the well-known acyl azides. Nevertheless, it was noted that Wieland had observed that triphenylmethylazide turns yellow with decomposition at its melting point. This is the color of phenylimido-benzophenone, the product of rearrangement anticipated by us. Experiment showed, without difficulty, that triphenylmethylazide does indeed form this product in good quantity when it is heated, the rearrangement proceeding as indicated in Equation 1. The phenylimido-benzophenone was identified by its products of hydrolysis, aniline and benzophenone formed under the influence of acids.



As a further main object of the present investigation, it was proposed to examine substitution derivatives of this azide, such as  $(\text{XC}_6\text{H}_4)(\text{C}_6\text{H}_5)_2\text{C}.\text{N}_3$  and  $(\text{XC}_6\text{H}_4)(\text{YC}_6\text{H}_4)(\text{C}_6\text{H}_5)\text{C}.\text{N}_3$ . In the rearrangement of the intermediate univalent nitrogen derivatives, in some of the molecules the phenyl radical would presumably migrate from the carbon to the nitrogen. In other molecules the derived radical  $(\text{XC}_6\text{H}_4)$  or  $(\text{YC}_6\text{H}_4)$ , would be the migrating group. For a mono substitution product we should have the simultaneous rearrangements

<sup>1</sup> Beckmann, *Ber.*, 19, 988 (1886); 27, 300 (1894); Hoogewerff and van Dorp, *Rec. trav. chim.*, 8, 173 (1889); Hantzsch, *Ber.*, 24, 3516 (1891); Kuhara, *Mem. Coll. Sci. Eng., Kyoto*, 1, 254 (1908); 2, 368 (1909-1910); 6, 1 (1913); *Ibid.*, 1, 25 (1914); cf. Stieglitz and Stagner, *Loc. cit.*

<sup>2</sup> *J. prakt. Chem.*, 63, 428 (1901); *Ber.*, 35, 3229 (1902).

<sup>3</sup> *Ber.*, 42, 3020 (1909). Wieland did not look for any molecular rearrangement.



and



A determination of the ratio in which the groups migrate in a given case seemed of particular importance for the purpose of comparing such a ratio with the results obtained from similar studies of the rearrangement of the corresponding compounds in the triphenylmethyl hydroxylamine and halogenamine series. All these series should give, according to Stieglitz's theory, the same intermediate product  $(\text{XC}_6\text{H}_4)(\text{C}_6\text{H}_5)_2\text{C.N}$  and might well show the same ratio of migrating radicals in spite of the difference in environment (temperature, reagents, etc.), since the rearrangement of the univalent nitrogen derivative is an intramolecular reaction. The time at my disposal has permitted the exhaustive investigation of only one instance of this kind, namely the rearrangement of *p*-chlorophenyldiphenylmethylazide. I found that in 68.1% of the rearranging molecules the phenyl radical migrates to the nitrogen, in 31.9% the chlorophenyl group is the migrating one. For the corresponding *p*-chlorophenyldiphenylmethylhydroxylamine, Leech<sup>1</sup> obtained the ratio 70.8/29.2. These results compare very favorably with mine. A broader basis of comparison between the series will ultimately be necessary, if coincidences are to be excluded.

It is evident that, thus far, the triarylmethylazides behave qualitatively and quantitatively like the corresponding triarylmethylhydroxylamines—a result, which is decidedly in favor of the Stieglitz theory of these molecular rearrangements, and against the Beckmann theory of a direct exchange of the migrating groups.

#### Experimental Part.

**Triphenylmethylhydrazine Hydrochloride**,  $(\text{C}_6\text{H}_5)_3\text{CNH.NH}_2.\text{HCl}$  and **Symmetrical Bis-Triphenylmethylhydrazine**,  $(\text{C}_6\text{H}_5)_3\text{CNH.NHC}(\text{C}_6\text{H}_5)_3$ .—Some attempts to prepare the first of these substances by the method described by Wieland<sup>2</sup> were unsuccessful. The source of this unexpected failure was not sought, instead the following alternative procedure which gave satisfactory results was developed. Triphenylmethylchloride was prepared according to the method of Gomberg.<sup>3</sup> Hydrazine hydrate (8 g.) and triphenylmethylchloride (21 g., 95% pure) were boiled in the presence of 60 cc. of absolute ether in a flask fitted with a reflux condenser. After a few hours, a precipitate appeared, and in ten hours the reaction was complete. The contents of the flask were then filtered and the precipitate, chiefly *bis*-triphenylmethylhydrazine, washed with ether and with water. The ethereal filtrate was shaken twice with water to remove

<sup>1</sup> THIS JOURNAL, 36, 272 (1914).

<sup>2</sup> Ber., 42, 3021, 3025 (1909).

<sup>3</sup> Ibid., 33, 3147 (1900).



traces of hydrazine hydrochloride, and the ether layer then dried over calcium chloride. To the dried ethereal solution a strong solution of dry hydrogen chloride in anhydrous ether was added. The triphenylmethylhydrazine hydrochloride was precipitated as a gummy mass, which, on being scratched, quickly turned granular. The flask was cooled in ice for half an hour and the precipitate then collected in a filter and dried. The yield was 11.5 g. of substance, melting at 108–113°.

The compound was analyzed by titration according to the Volhard method.

0.2469 g. subs. required 7.89 cc. of 0.1 *N* AgNO<sub>3</sub>.

Calc. for C<sub>18</sub>H<sub>15</sub>N<sub>2</sub>HCl: HCl, 11.74. Found: 11.65.

Analyses of many samples prepared by this method always showed that the substance was nearly pure. It was, therefore, used without further refinement. Attempts to purify it by recrystallization from absolute alcohol and ether, according to the method of Wieland, failed in every case. The substance was always rapidly "alcoholized" by the solvent.

The precipitate formed in the flask when the hydrazine hydrate and triphenylmethylchloride were boiled together was symmetrical *bis*-triphenylmethylhydrazine. After it had been washed with ether and water on the filter, it was removed and boiled with alcohol, collected again on a filter and dried. The yield was 4 g. of material melting at 205°. The substance was further purified by the method of Wieland.<sup>1</sup> When pure, it melted at 210°.

**Triphenylmethylazide, (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>CN<sub>3</sub>.**—This compound was prepared from triphenylmethylhydrazine hydrochloride according to the method of Wieland.<sup>2</sup> The crude reaction product melting at 57° was used for the rearrangements. A small portion, recrystallized from alcohol, melted at 61°.

**Rearrangement of Triphenylmethylazide.**—Two portions of triphenylmethylazide of 0.5 g. each were heated in sealed tubes at 225° for one hour. The tarry product of the reaction was examined for the expected rearrangement product, phenylimido-benzophenone, as follows: it was extracted with about 20 cc. of benzene and the extract evaporated to dryness in a flask on the steam bath. No attempt was made to first to isolate the pure phenylimido-benzophenone from the residue thus obtained; instead, it was hydrolyzed and identified by its decomposition products, aniline and benzophenone. For this purpose this residue was dissolved in alcohol, a little hydrochloric acid was added to the solution, and the mixture boiled for half an hour in a flask fitted with a reflux condenser. Excess of sodium hydroxide was then added to the solution, and the liquid distilled with steam to isolate the aniline and benzophenone

<sup>1</sup> *Loc. cit.*

<sup>2</sup> *Ber.*, 42, 3027 (1909).

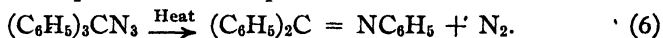
formed. The milky distillate gave a strong purple color with hypochlorite. It was acidified, the solution washed with ether to remove benzophenone, and the aqueous solution evaporated. It yielded 0.276 g. of substance, equivalent to 60% of the aniline hydrochloride, which could, theoretically, be obtained from the rearrangement of the amount of azide used. From the hydrochloride, the chloroplatinate of aniline was obtained and analyzed.

(I) 0.3772 and 0.1278 g. subs. gave 0.1258 and 0.0413 g. Pt.

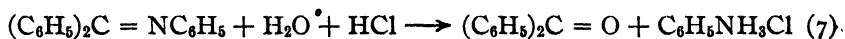
Calc. for  $C_{12}H_{16}N_2PtCl_6$ : Pt, 32.75%. Found: (I) 33.35; (II) 32.32.

The ether extract of the acidified steam distillate on evaporation to dryness gave an oily residue. When this was seeded with a tiny crystal of benzophenone it quickly crystallized. The solid, after recrystallization from alcohol and water, melted at 47–47.5°. A mixture of this substance with benzophenone (melting point 47–47.5°) also melted at 47–47.5°.

These results identify the products of hydrolysis of the chief end product of the action of heat on triphenylmethylazide as aniline and benzophenone. These are the products of hydrolysis of phenylimido-benzophenone. Triphenylmethylazide undergoes rearrangement therefore under the influence of heat, as expressed in the equation



The phenylimido-benzophenone produced is then hydrolyzed by the dilute acid:



Attempts to isolate the intermediate phenylimido-benzophenone were given up on account of the large proportion of tarry products present.

***p*-Chlorophenyl-diphenylmethylhydrazine Hydrochloride**,  $(C_6H_4Cl)-(C_6H_5)_2C.NH.NH_2.HCl$ .—Dichlorodiphenylmethane,  $(C_6H_5)_2C.Cl_2$ , was prepared according to Mackenzie,<sup>1</sup> and from it *p*-chlorophenyl-diphenylmethylchloride was obtained by the method of Gomberg.<sup>2</sup> The substance used in the preparations to be described melted at 86°. It was analyzed by hydrolysis with standard alkali.

Calc. for  $C_{19}H_{14}Cl_2$ : hydrolyzable Cl, 11.33%. Found: 11.27.

In the preparation of *p*-chlorophenyl-diphenylmethylhydrazine hydrochloride and symmetrical *bis-p*-chlorophenyl-diphenylmethylhydrazine, the proportions of *p*-chlorophenyl-diphenylmethylchloride and hydrazine hydrate used must be varied according to which of these two products is desired. The method used to obtain the mono derivative is given here.<sup>3</sup> *p*-Chlorophenyl-diphenylmethylchloride (5.75 g.) and hydrazine hydrate (4 g.) were boiled with a small amount of absolute ether in a flask fitted

<sup>1</sup> *J. Chem. Soc.*, 69, 987 (1896).

<sup>2</sup> *Ber.*, 37, 1633 (1904).

<sup>3</sup> The preparation of the *bis*-derivative is described in the following paper.

with a reflux condenser. The hydrazine hydrate did not dissolve in the ether, and the two layers of liquid persisted till the end of the reaction. After a few hours a precipitate appeared, and at the end of eight hours the reaction was finished. The flask was stoppered and allowed to stand overnight. The reaction mixture was then poured through a filter moistened with absolute ether on a Hirsch funnel. The filtrate consisted of two layers. The upper layer was an ethereal solution of *p*-chlorophenyl-diphenylmethylhydrazine and the lower was a mixture of hydrazine hydrate and hydrazine hydrochloride. The ethereal layer was dried over calcium chloride and then an excess of dry hydrogen chloride in absolute ether was added to the solution. After a few minutes, a heavy precipitate of *p*-chlorophenyl-diphenylmethylhydrazine hydrochloride appeared. The flask was cooled in ice for about 15 minutes and the solid then collected on a filter and dried on a clay plate. It melted at 122°. The yield was 4 g.

The compound is not very stable. It is slowly decomposed by the moisture of the air, and all attempts to purify it by recrystallization failed. Consequently the crude substance was used to prepare the azide. It was analyzed by titration by the Volhard method.

0.1524 g. subs. required 4.91 cc. of 0.1 *N* AgNO<sub>3</sub>.

Calc. for C<sub>15</sub>H<sub>17</sub>ClN<sub>2</sub>HCl: HCl, 10.57. Found: 11.75.

A small amount of symmetrical *bis-p*-chlorophenyl-diphenylmethylhydrazine was always formed during the boiling of the *p*-chlorophenyl-diphenylmethylchloride with hydrazine hydrate. It crystallized out of the reaction mixture and was removed by the filtration on the Hirsch funnel. It was washed with alcohol and water to remove adhering traces of hydrazine, etc., and then dried. The yields were always small. The compound melted at 201°.

***p*-Chlorophenyl-diphenylmethylazide**, (C<sub>6</sub>H<sub>4</sub>Cl)(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>CN<sub>3</sub>.—For the preparation of this azide 4.8 g. of the corresponding hydrazine hydrochloride were dissolved in 60 cc. of absolute alcohol, and to this solution were added 30 cc. of hydrochloric acid, containing 7 g. of hydrogen chloride per 100 cc. of the acid. The flask was immersed in ice and 20 cc. of sodium nitrite solution, containing 1.6 g. of sodium nitrite, were run slowly into the solution while the flask was constantly shaken. The original solution in alcohol and acid was clear, but as the sodium nitrite was run in, the solution became cloudy and, on standing a few hours in the cold, the milky emulsion settled out at the bottom of the vessel as a yellowish gum. After the aqueous liquid had been decanted, the gum was dissolved in ether and the solution dried over calcium chloride. When the ether was boiled off, the yield of gum was 3.75 g.

All attempts to crystallize the material were unsuccessful. A variety of solvents and extreme cold were tried without avail. No analyses

were therefore attempted, and the crude substance was used directly for rearrangement.

**Rearrangement of *p*-Chlorophenyl-diphenylmethylazide.**—A solution of 3.75 g. of *p*-chlorophenyl-diphenylmethylazide in ether was placed in a hard glass test-tube, the ether was boiled out, and the tube containing the gum heated in a metal bath. At about 185° a fairly active evolution of gas began. The temperature was slowly raised until 215° was reached at the end of about ten minutes. The tube was then cooled, and the tarry mass examined for the products of rearrangement, phenylimido-chlorobenzophenone and chlorophenylimido-benzophenone, by the isolation of the products of hydrolysis of these two imides. The mass was extracted with ether, the ether extract transferred to a flask and the ether boiled off on the steam bath. About 30 cc. of alcohol and a little hydrochloric acid were added to the residue and the mixture boiled for half an hour with a reflux condenser. The liquid was then made alkaline with sodium hydroxide and distilled with steam. The distillate was a milky liquid containing oily drops which crystallized in standing. With hypochlorite it gave a strong purple color. It was acidified with hydrochloric acid, to convert the anilines into their salts, the ketones were removed by extraction with ether, and the ether extract (A) separated from the aqueous solution (B). The rearrangement was found to be far from quantitative<sup>1</sup> and on account of the small yields some difficulty was experienced in identifying the products. \*

(A) **Identification of Benzophenone and *p*-Chlorobenzophenone.**—The ether extracts (A) of the acidified steam distillates of several reactions like the one described above were combined. The ether was dried over calcium chloride and evaporated in an open dish. A crystalline residue was left. About three-fourths of this residue was dissolved by alcohol. The remainder, when dried on a clay plate, melted at 71–72°. When this substance was mixed with *p*-chlorobenzophenone (melting point 74.5–75.5°), the mixture melted at 72.5–73.5°. These results established the identity of this fraction of the unknown substance with *p*-chlorobenzophenone.

Attempts to isolate pure benzophenone from the alcoholic solution were unsuccessful. Efforts were made to use the fact that benzophenone is much more soluble than *p*-chlorobenzophenone in cold ligroin (boiling point 30–50°). The alcoholic solution was evaporated to dryness, extracted with ligroin, and the extract evaporated to dryness. The crystalline residue was again extracted with ligroin and the ligroin evaporated. The process was repeated once more. On evaporation, the final ligroin solution left behind the roset-shaped aggregates characteristic of *p*-chloro-

<sup>1</sup> Attempts to improve the yield by the use of acids and other reagents will be made in this laboratory.

benzophenone, and a few drops of oily liquid. When these drops were seeded with a tiny crystal of benzophenone, they crystallized. This action, often observed in this laboratory to be characteristic of benzophenone, was taken as an indication that the oily droplets consisted of benzophenone, but there was not enough pure material to confirm the conclusion.

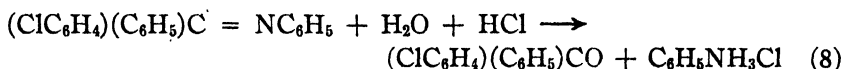
(B) **Identification of Aniline and *p*-Chloroaniline.**—After the steam distillates of several reactions like the one described above had been acidified and extracted with ether, the aqueous solutions (B) were combined, made alkaline with excess sodium hydroxide and again extracted with ether. The ether extract was acidified with a little aqueous hydrochloric acid and evaporated to dryness. A white crystalline residue of hydrochlorides of aniline bases was left. This was divided into several portions and treated as follows:

(1) One portion was dissolved in water, made alkaline with sodium hydroxide and extracted with ether. The ether extract was dried over anhydrous potassium carbonate. To it was then added a solution of anhydrous oxalic acid in absolute ether. The white crystalline precipitate which immediately formed was filtered out, dried, and dissolved in a small amount of hot water containing a little oxalic acid. When the liquid was cooled, a precipitate appeared. This oxalate was brought on a filter and dried. The mother liquor gave with hypochlorite a strong purple color, showing definitely the presence of aniline in the original mixture. The oxalate just described was dissolved in a very little water, and to the solution a few drops of ammonia were added. An oil immediately separated, which, on standing a few minutes, solidified. The solid was brought on a filter and dried on a clay plate. It melted at  $67.5^{\circ}$ . When this substance was mixed with *p*-chloroaniline (melting point  $70.5^{\circ}$ ) the mixture melted at  $69.5^{\circ}$ . These results showed that this fraction of the unknown substance was *p*-chloroaniline. When burned on a clean copper wire, it gave a green flame, confirming the presence of halogen (chlorine).

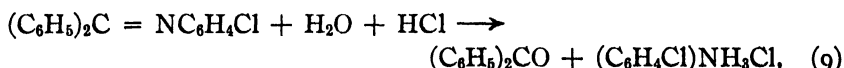
(2) Another portion of the dry hydrochlorides described under (B) was dissolved in absolute alcohol and, after filtration of the solution, the hydrochlorides were reprecipitated by the addition of absolute ether containing a small amount of dry hydrogen chloride. The precipitate was collected and dried on a clay plate. From it were taken Samples I and II for the analyses given below under C. The alcohol-ether mother-liquor was evaporated to dryness, the residue taken up with absolute alcohol and the hydrochlorides again precipitated by means of absolute ethereal hydrochloric acid. This second precipitate was collected and dried as before. From it, analysis Sample III was taken.

(3) A third portion of the dry hydrochlorides described under (B) was treated like the portion (2), except that the precipitation process was carried out a third time. All three yields of precipitate in this case were combined, and from the mixture, analysis Sample IV was taken.

The qualitative results thus far obtained have shown that products of the action of heat on *p*-chlorophenyl-diphenylmethylazide yield on hydrolysis chlorobenzophenone and benzophenone besides aniline and chloroaniline. These are the products to be expected from the hydrolysis of phenylimido-chlorobenzophenone



and chlorophenylimido-benzophenone



the two imido ketones which are the anticipated products of the rearrangement of the azide (see Equations 3 and 4).

(C) **The Determination of the Ratio of the Rearrangement Products.**—A determination of the ratio in which the two imidoketones are formed was a matter of considerable theoretical interest (see the theoretical part of this paper). For this reason the molecular proportions of the hydrochlorides of the two bases were next determined, the samples enumerated under (B) being analyzed volumetrically by the bromination method of Curme.<sup>1</sup>

	Mixed hydrochloride.	0.1N KBrO <sub>3</sub> required.	Molecular % aniline.	Molecular % <i>p</i> -chloroaniline.
(I)	0.0384 g.	14.75 cc.	69.2	30.8
(II)	0.0415	15.68	66.5	33.5
(III)	0.0221	8.14	62.4	37.6
(IV)	0.0418	16.15	74.1	25.9
			Average, 68.1	31.9

The proportions in which the pair of rearrangement products of *p*-chlorophenyl-diphenylmethylazide are formed are very close to those found by Leech for *p*-chlorophenyl-diphenylmethylhydroxylamine (70.8/29.2).

In conclusion I wish to express my gratitude to Professor Stieglitz under whose direction this work was done, and to whom I am much indebted for the kind assistance and advice which enabled me to carry it out.

CHICAGO, ILL.

<sup>1</sup> THIS JOURNAL, 35, 1143 (1913).

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO,]

# THE MOLECULAR REARRANGEMENT OF *sym.-bis*-TRIARYLMETHYLHYDRAZINES.<sup>1</sup> PRELIMINARY REPORT.

BY JULIUS STIEGLITZ AND JAMES KUHN SENIOR.<sup>2</sup>

Received September 21, 1916.

The fundamental analogy between hydroxylamine and hydrazine is a well-established fact,<sup>3</sup> equally evident from the reactions of the substances and from the parallelism existing between their organic derivatives, a parallelism which extends even to the formation of stereoisomeric oximes and hydrazones.<sup>4</sup> It seems to have escaped comment, however, that in one important respect there exists a gap between the chemistry of hydroxylamine derivatives and that of the corresponding derivatives of hydrazine. Hydroxamic acids<sup>5</sup>  $\text{RCO.NHOH}$ , dihydroxamic acids  $\text{RCO.NHO.COR}$ , ketoximes<sup>7</sup>  $\text{R}_2\text{C} : \text{NOH}$ , and triphenylmethylhydroxylamines<sup>8</sup>  $\text{R}_3\text{C.NHOH}$ , under the influence of appropriate reagents, readily undergo molecular rearrangements in which a radical R migrates from the carbon atom originally holding it to the neighboring nitrogen atom. Similar rearrangements<sup>9</sup> of hydrazine derivatives have never been observed or even attempted, as far as we can find. It is worthy of note, too, that even derivatives of hydrogen peroxide, the third member<sup>10</sup> of the hydrazine-hydroxylamine family,<sup>11</sup> undergo rearrangements analogous to those of the hydroxylamine derivatives; this fact has been observed, for instance,

<sup>1</sup> A brief statement was published in *Proc. Nat. Acad. Sciences*, **1**, 207 (1915).

<sup>2</sup> The work in this paper forms the basis, in part, of a dissertation presented to the University of Chicago in fulfillment of the requirement for the Ph.D. degree.

<sup>3</sup> See, for instance, Angeli, *Chem. Zentr.*, **1910**, II, 861; Stieglitz and Curme, *Ber.*, **46**, 911 (1913).

<sup>4</sup> Hantzsch and Kraft, *Ber.*, **24**, 3516 (1891).

<sup>5</sup> Lossen, *Ann.*, **161**, 359 (1872), etc.

<sup>6</sup> Lossen, *Ibid.*; L. W. Jones, *Am. Chem. J.*, **48**, 1 (1912).

<sup>7</sup> Beckmann, *Ber.*, **19**, 988 (1886); **27**, 300 (1894), etc.

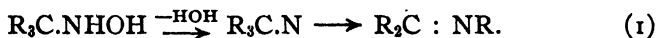
<sup>8</sup> Stieglitz, Reddick and Leech, *Eighth Intern. Congr. Appl. Chem.*, **25**, 443 (1912); Stieglitz and Leech, *Ber.*, **46**, 2147 (1913); *THIS JOURNAL*, **36**, 272 (1914); Stieglitz and Stagner, *Ibid.*, **38**, 2046 (1916); Stagner, *Ibid.*, **38**, 2069 (1916), and Vosburgh, *Ibid.*, **38**, 2081 (1916).

<sup>9</sup> The benzidine and related rearrangements are of a different type, although arising no doubt from the same source of instability in the molecules involved (see Stieglitz and Stagner, *THIS JOURNAL*, **38**, 2051 (1916).

<sup>10</sup> Cf. Angeli, *Loc. cit.*; Stieglitz and Curme, *Loc. cit.*; Stieglitz and Leech, *Loc. cit.*

<sup>11</sup> The list might well be extended to include hypochlorous, hypobromous and hypoiodous acids and their derivatives. The members have as a common characteristic an atom with an unstable positive charge and a tendency to convert this atom into the common, stable negative variety.

in the cases of ketone peroxides<sup>1</sup> and triphenylmethyl peroxide.<sup>2</sup> The fundamental analogy between hydrazines, hydroxylamines and peroxides suggested the desirability of investigating hydrazine derivatives from this point of view, and of attempting to close the gap which at present exists between these groups in this one respect. The theory of one of us as to the mechanism and cause of the molecular rearrangements of this type made it appear altogether likely that similar rearrangements might be brought about without great difficulty in hydrazine derivatives. As is known, according to this theory,<sup>3</sup> the rearrangement of a triarylmethylhydroxylamine, for instance, is considered to be due to the formation of a univalent nitrogen derivative by the loss of water, or its equivalent, under the influence of a dehydrating agent like phosphorus pentachloride.



To effect the rearrangement of the corresponding hydrazines, it seemed only necessary to use a suitable reagent to induce the loss of ammonia.



From the point of view of the electronic theory of valence, we consider<sup>4</sup> that the primary force leading to the rearrangement of hydroxylamine derivatives<sup>5</sup> resides in the *unstable positive charge* on the oxygen atom.<sup>6</sup> There must be a great tendency of the positive hydroxyl group to go over into its common, stable negative form, as it does, if water or its equivalent is taken from the hydroxylamine derivative by dehydrating agents. We have

<sup>1</sup> Baeyer, *Ber.*, 32, 3627 (1900). The relation of the peroxide rearrangement to the rearrangements of hydroxylamine derivatives was first recognized by Baeyer, but both were given a wrong interpretation (see Stieglitz, *Am. Chem. J.*, 29, 49 (1903); and Stieglitz and Stagner, *Loc. cit.*). Especially the results in this laboratory on the rearrangements of triphenylmethane derivatives make Baeyer's assumptions quite untenable. The peroxides have now been included in our studies of the theory from the point of view of the one of us.

<sup>2</sup> Wieland, *Ber.*, 44, 2350 (1911).

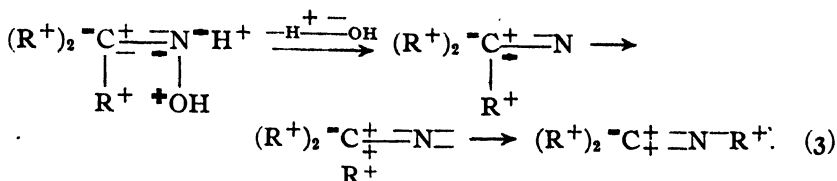
<sup>3</sup> The literature references are given by Stieglitz and Leech, *Loc. cit.*, and Stieglitz and Stagner, *Loc. cit.*

<sup>4</sup> The electronic version of the univalent nitrogen theory of one of us for this and analogous rearrangements is found in detail in *THIS JOURNAL*, 36, 272 (1914). While the article was in press an article by L. W. Jones appeared (*Am. Chem. J.*, 50, 440 (1913)), giving an interpretation of this theory, differing from the Stieglitz views in some important details, but agreeing with them in the fundamental considerations. See footnote, *THIS JOURNAL*, *Loc. cit.*, p. 287.

<sup>5</sup> Stieglitz and Leech, *Loc. cit.*

<sup>6</sup> For the rearrangement of the closely related chloroamines similar relations hold, as expressed by Stieglitz and Leech, *Ber.*, 46, 2147 (1913).



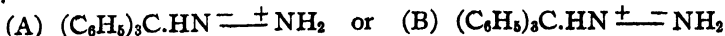


The shifting of electrons is indicated by heavy type for the charges which are about to undergo change.

In hydrazines,  $\text{H}_2\text{N}^+ \text{---} \text{NH}_2$ , there is likewise an unstable positive group,<sup>1</sup> which should have a decided tendency to go over into the stable negative radical  $\text{N} \equiv$  as it exists in ammonia  $\text{N} \equiv (\text{H}^+)_3$ . If this tendency showed itself in the loss of ammonia by certain hydrazine derivatives, it might lead to a series of reactions similar to those just described and ending in the postulated molecular rearrangement.

From this point of view the reagents that suggest themselves for effecting such rearrangements are strong acids and zinc chloride. To our disappointment, not a single rearrangement of this character was observed in studying the effect of concentrated sulfuric acid on a great variety of hydrazine derivatives.<sup>2</sup> Simple hydrolysis or sulfonation was the only reaction detected. The heating of dry hydrochlorides of hydrazine derivatives was no more effective in producing rearrangements.

Although these experiments were preliminary ones, they were sufficiently extensive and thorough to make us pause and consider the theoretical relations in greater detail. In the case of the hydroxylamine derivatives which undergo rearrangement, there can be no question as to the distribution of the original charges—the hydroxyl in hydroxylamine  $\text{H}_2\text{N} \text{---} \overset{+}{\text{OH}}$  is originally positive and ultimately forms water (or its equivalent) with a negative hydroxyl group.<sup>3</sup> For the substituted hydrazines, however, we have as yet no trustworthy basis for determining the exact electronic structure.<sup>4</sup> A single illustration will make the point clear: triphenylmethylhydrazine may have either of two electronic structures:



Either one, according to the mechanism of the possible loss of ammonia, might account for the failure of acids to induce the loss of ammonia and subsequent rearrangement. In B, for instance, the  $\text{NH}_2$  group is already negative and in its most stable electronic structure, and so the funda-

<sup>1</sup> Stieglitz and Curme, *Ber.*, **46**, 911 (1913).

<sup>2</sup> Some of these experiments and their results will be described later by Mr. Senior.

<sup>3</sup> See the evidence given by Stieglitz, *THIS JOURNAL*, **36**, 288 (1914), and by Jones, *Ibid.*, **36**, 1268 (1914).

<sup>4</sup> In the salts the wholly negative nitrogen atom is probably the one that is combined with the acid, but this does not help us toward a solution of the problem before us.

mental force leading to its elimination from the molecule as ammonia with the subsequent rearrangement of the organic radical might well be altogether lacking.<sup>1</sup> These considerations made it appear desirable to attempt the rearrangement of a *symmetrical molecule*, bis-triphenylmethylhydrazine, about whose electronic structure there can be no doubt:  $(\text{C}_6\text{H}_5)_3\text{C.NH}^+ \text{---} \text{NH.C}(\text{C}_6\text{H}_5)_3$ . A loss of triphenylmethylamine from *either side* would yield a univalent nitrogen derivative  $(\text{C}_6\text{H}_5)_3\text{C.N}$  and rearrangement should inevitably follow. Whether this argument is ultimately found to be right or wrong, it certainly is of peculiar interest that in this instance we were at last successful in effecting a rearrangement. Zinc chloride was the agent used. The occurrence of a rearrangement was proved by the isolation and identification of aniline as a product of the action: aniline could be formed only by a migration of a phenyl radical from carbon to nitrogen—the typical migration of this class of molecular rearrangements. As far as we can discover, this is the first time any hydrazine derivative has been observed to rearrange in this fashion. *sym.-bis-p*-Chlorophenyl-diphenylmethylhydrazine,  $(\text{ClC}_6\text{H}_4)(\text{C}_6\text{H}_5)_2\text{C.NH.NHC}(\text{C}_6\text{H}_5)_2(\text{C}_6\text{H}_4\text{Cl})$ , has been found by us to suffer the same rearrangement, producing aniline and, probably, *p*-chloroaniline as well. This agrees with the results obtained in the molecular rearrangements of *p*-chlorophenyl-diphenylmethylhydroxylamine  $(\text{ClC}_6\text{H}_4)(\text{C}_6\text{H}_5)_2\text{C.NHOH}$  and the corresponding chloroamine  $(\text{ClC}_6\text{H}_4)(\text{C}_6\text{H}_5)_2\text{C.NHCl}$ .

As to the mechanism of the rearrangement of the hydrazine we can state nothing positive, since the action is not a smooth one and the products, other than aniline and triphenylmethane, a product of a parallel reaction, have not, as yet, been identified. It is altogether likely, however, that the rearrangement is the result either of a primary dissociation into a univalent nitrogen derivative, along the lines indicated above, or of a dissociation into bivalent nitrogen radicals, according to

$$\begin{array}{c}
 (\text{C}_6\text{H}_5)_3\text{CNH.NHC}(\text{C}_6\text{H}_5)_3 \longrightarrow 2(\text{C}_6\text{H}_5)_3\text{C.NH} \longrightarrow 2(\text{C}_6\text{H}_5)_2\text{C.NHC}_6\text{H}_5 \\
 \begin{array}{c} | \\ (\text{C}_6\text{H}_5)_2\text{C.NHC}_6\text{H}_5 \end{array} \qquad \qquad \qquad \begin{array}{c} | \\ (\text{C}_6\text{H}_5)_2\text{C.NHC}_6\text{H}_5 \end{array} \\
 \begin{array}{c} | \\ (\text{C}_6\text{H}_5)_2\text{C.NHC}_6\text{H}_5 \end{array}
 \end{array}
 \tag{4}$$

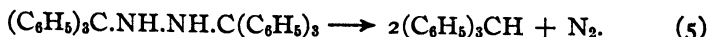
The latter reaction would correspond to the molecular rearrangement of triphenylmethylperoxide under the influence of heat, as observed and interpreted by Wieland.<sup>2</sup> It may be remarked in this connection that, in the case of the rearrangement of  $\beta$ -triphenylmethyl- $\beta$ -methylhydroxylamine, where the same alternative was presented, exhaustive examina-

<sup>1</sup> A decomposition  $(\text{C}_6\text{H}_5)_3\text{C.NH} \text{---} \text{NH}_2 \longrightarrow (\text{C}_6\text{H}_5)_3\text{C.NH}_2 + (\text{NH})$  would not lead to a rearrangement. This would hold either for A or B.

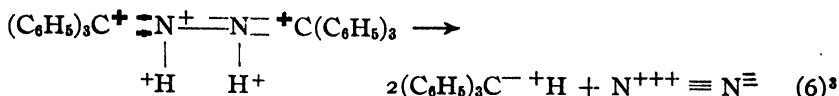
<sup>2</sup> *Loc. cit.*

tion of the secondary products finally decided against this type of rearrangement for the hydroxylamine compound in question.<sup>1</sup>

The formation of triphenylmethane is probably the result of a parallel decomposition of the symmetrical hydrazide, as expressed in the equation



The reaction is of some interest from the electronic point of view. We have:<sup>2</sup>



According to this equation, the instability of the radical  $\equiv\text{N}^+$  leads to a breakdown of the molecule, in which the extraordinarily stable nitrogen is formed by a transfer of electrons to (*i. e.*, reduction of) the methyl carbon atoms.<sup>4</sup>

### Experimental Part.<sup>5</sup>

*sym.-bis-Triphenylmethylhydrazine*,  $(\text{C}_6\text{H}_5)_3\text{CNH.NHC}(\text{C}_6\text{H}_5)_3$ .—The compound was prepared according to the method described by one of us,<sup>6</sup> and purified by the method of Wieland.<sup>7</sup> The substance used for rearrangement melted at 210°.

**Rearrangement of *sym.-bis-Triphenylmethylhydrazine*.**—One gram of the substance was triturated with 6 g. of anhydrous zinc chloride in a warm mortar. The mixture turned bright yellow. It was transferred to a hard glass test-tube and heated in a metal bath at 300° for ten minutes. After the tube had been cooled, the dark-colored melt was dissolved out with ether and water. Sufficient sodium hydroxide was added to get all the zinc into alkaline solution and the liquid was then shaken twice

<sup>1</sup> Stieglitz and Stagner, *THIS JOURNAL*, 38, 2046 (1916).

<sup>2</sup> The electronic structure given to free nitrogen is simply illustrative. The formula used agrees with the formation of nitrogen from ammonia and nitrous acid, but the reversed action, the saponification of nitrogen (nitrous acid nitril) does not seem to have been accomplished as yet. Free energy calculations, made at the suggestion of Professor G. N. Lewis, indicate, as anticipated, that the hydrolysis would involve the absorption of a great deal of energy. The combination of nitrogen, as a substituted amine, has also not yet been accomplished, although preliminary experiments to combine it with hydrogen chloride were made by one of us some years ago. An investigation of these problems and of the electronic structure of nitrogen is being undertaken.—J. S.

<sup>3</sup> The electronic changes are indicated by heavy type.

<sup>4</sup> The decomposition of the hydrazide in this direction is being further investigated by Mr. R. L. Brown.

<sup>5</sup> I am glad to take this opportunity to thank my young collaborator for his painstaking experimental work and tenacious energy in an investigation that at first brought only disappointing results.—J. S.

<sup>6</sup> See the preceding article.

<sup>7</sup> *Ber.*, 42, 3022 (1909).

in a separatory funnel with ether. The ether layers were combined, transferred to a flask, and the ether boiled off on the steam bath. A tarry residue remained behind. With the object of having any aniline derivative present hydrolyzed, this residue was dissolved in alcohol and some hydrochloric acid added to the solution, which was then boiled for half an hour under a reflux condenser. Excess of sodium hydroxide was next added, and the mixture steam distilled. The cloudy distillate was collected in two portions. The first portion gave a strong purple color with hypochlorite, thus showing the presence of aniline. When the droppings ceased to give this test, the receiver was changed. Throughout the distillation a white solid (later identified as triphenylmethane) was deposited in the condenser. When this substance ceased to come over, distillation was stopped. The first portion of the distillate was acidified with hydrochloric acid and extracted with ether, the acid solution (A) being preserved for further investigation. The second portion of the distillate was also extracted with ether, and the water layer discarded. The two ether extracts were combined and to them was added the ethereal solution of the solid which collected in the condenser.

The acid solution (A) of the first distillate, on evaporation, yielded a small amount of white crystalline residue. From the qualitative tests, the substance was presumed to be aniline hydrochloride. For the quantitative study, the process described had to be repeated several times to obtain sufficient material for analysis. When this material was treated with chloroplatinic acid, the precipitate was found to be pure aniline chloroplatinate.

0.1375 g. subs. gave 0.0451 g. Pt. Calc. for  $C_{12}H_{18}N_2PtCl_6$ : Pt, 32.75. Found: 32.80.

The combined ether extracts of the distillate were dried over calcium chloride and the ether then evaporated. There was left a gummy residue which, on being scratched, quickly crystallized. The crystals, when dried on a clay plate, melted at  $79-81^\circ$ . When the yields of several experiments such as the one described above had been collected, the substance was crystallized from alcohol. After two recrystallizations, the compound apparently had a constant melting point of  $81.5-82^\circ$ .

(I) 0.1496 and 0.1620 g. subs. gave 0.0834 and 0.0903 g.  $H_2O$  and 0.5062 and 0.5476 g.  $CO_2$ . Calc. for  $C_{18}H_{18}$ : C, 93.40; H, 6.60. Found: (I) C, 92.28 and 92.19; H, 6.24 and 6.24.

Qualitative and quantitative (combustion) tests showed the absence of nitrogen, and a qualitative test for halogen also proved negative. The melting points of mixtures showed that the material was neither triphenylcarbinol nor triphenylmethylether, which might have been formed by hydrolysis or alcoholysis of the hydrazine or of one of its decomposition products. A mixture of equal quantities of triphenylmethane (m. p.  $89-90^\circ$ ) and the substance, melted at  $85-89^\circ$ , and a mixture of four parts of the substance with one part of triphenylmethane showed no depression

of the melting point of the substance. The compound gave the (spectroscopic) *p*-rosaniline test for triphenylmethane. The substance seems therefore to be somewhat impure triphenylmethane.<sup>1</sup>

In an effort to obtain a smoother rearrangement and reaction, attempts were made to rearrange *sym.-bis-triarylmethylhydrazine* by heat (in a sealed tube) and also by the action of dry hydrogen chloride at 300°. In both cases the substance was decomposed, but no trace of aniline could be found in the hydrolyzed reaction products. The reactions were not further investigated.<sup>2</sup>

*sym.-p-Chlorophenyl-diphenylmethylhydrazine*,  $(C_6H_4Cl)(C_6H_5)_2CNH.NHC(C_6H_5)_2(C_6H_4Cl)$ .—Dichlorodiphenylmethane,  $(C_6H_5)_2CCl_2$ , was prepared according to Mackenzie,<sup>3</sup> and from it *p*-chlorophenyl-diphenylmethylchloride by the method of Gomberg.<sup>4</sup> The action of this chloride on hydrazine gives fair yields either of the mono-substituted hydrazine or of the *bis*-derivative, according to the conditions used. The preparation of the mono-derivative is described in the preceding article. For the preparation of the *bis*-derivative, *p*-chlorophenyl-diphenylmethylchloride (5.75 g.) and hydrazine hydrate (2 g.) were boiled for seven hours in the presence of a small amount of absolute ether in a flask fitted with a reflux condenser. A considerable amount of precipitate was formed. The mixture was filtered on a Hirsch funnel, the filter being wet with ether, and the precipitate washed with ether, water and alcohol to remove adhering impurities. When dried on a clay plate, it melted at 201°. Attempts were made to recrystallize this material by the same method as that used in the case of *sym.-bis-triphenylmethylhydrazine*. The substance was dissolved in hot benzene. On addition of warm alcohol it crystallized out. There was no apparent decomposition, but that some change had occurred was shown by the fact that the melting point of the substance was much lower than that of the original substance. Several repetitions of the process yielded a product melting at 171°. This substance was analyzed.

0.2903 g. subs. gave 0.1377 g. Ag Cl (Carius' method).

(I) 0.3610 g. subs. gave 5.12 cc. of  $N_2$  at 28.0° and 729.9 mm.; (II) 0.3727 g. gave 5.31 cc. at 28.8° and 729.1 mm.

Calc. for  $C_{28}H_{20}N_2Cl_2$ : Cl, 12.12; N, 4.79. Found: Cl, 11.73; N, (I) 1.54, (II) 1.54.

On account of the obvious decomposition encountered in the attempt to recrystallize it, the crude substance melting at 201° was next analyzed.

<sup>1</sup> To confirm this conclusion and especially to secure sufficient material for a molecular-weight determination, the preparation will be repeated as soon as occasion offers. (Since this was written, Mr. R. L. Brown has obtained the product as pure triphenylmethane, melting at 92°.—J. S.)

<sup>2</sup> They are now being investigated by Mr. R. L. Brown.

<sup>3</sup> *J. Chem. Soc.*, 69, 987 (1896).

<sup>4</sup> *Ber.*, 37, 1633 (1904).

0.3600 g. subs. gave 21.21 cc. of  $N_2$  at  $22.4^\circ$  and 740.1 mm.

Calc. for  $C_{18}H_{10}N_2Cl_4$ : N, 4.79. Found: 6.63.

The high nitrogen content of this crude substance melting at  $201^\circ$  was supposed to be due to an impurity of hydrazine. The substance was assumed for the present to be *sym.-bis-p-chlorophenyl-diphenylmethylhydrazine* and was used in a preliminary way as material for rearrangements. This compound and its decomposition product, melting at  $171^\circ$ , will be investigated further in this laboratory.

**Rearrangement of *sym.-bis-p-Chlorophenyl-diphenylmethylhydrazine*.**

—The rearrangement was carried out with the aid of zinc chloride in exactly the same way as described above for the corresponding chlorine-free compound. A considerable portion of the original melt was found to be insoluble in both ether and water. Steam distillation, after the hydrolysis of the product (see above), yielded a slightly cloudy distillate which gave a purple color with hypochlorite. No substance solidified in the condenser as in the case of the triphenylmethyl compound. The distillate was acidified with hydrochloric acid and shaken with ether. After the ether layer had been dried over calcium chloride, it was evaporated to dryness. The gummy residue left behind was so trifling in amount that it was not further investigated. The acidified water layer was evaporated to dryness. A small white crystalline residue was left behind. This was presumably a mixture of the hydrochlorides of aniline and *p*-chloroaniline.

When the yields of several reactions like the one described above had been collected and combined, the substance was dissolved in water, and a little sodium hydroxide added to the solution. The solution was shaken twice with ether, and the ether layer separated and dried over anhydrous potassium carbonate. To it was added an absolute ethereal solution of anhydrous oxalic acid. The precipitate formed was filtered out and dried on a clay plate. A small portion of it, when heated on a clean copper wire, gave a green flame, indicating that probably some *p*-chloroaniline was present. The main part of the precipitate was dissolved in a small amount of hot water containing a little oxalic acid. When the solution was cooled, a crystalline precipitate separated out. This was filtered off and dried. The mother liquor gave a strong purple color with hypochlorite, thus confirming the presence of aniline. The precipitate was dissolved in a little water and a few drops of ammonia added. The solution became cloudy, but the expected separation of solid *p*-chloroaniline did not occur. The solution was shaken with ether and the ether layer separated and evaporated to dryness. When the small gummy residue was scratched with a tiny crystal of *p*-chloroaniline, it crystallized. This indicated that the gum was probably impure *p*-chloroaniline, but the amount of material was too small to permit of further identification.

**Attempts to Rearrange Unsymmetrical Hydrazines and Hydrazones.**

A number of attempts were made to rearrange unsymmetrical hydrazines and hydrazones. These attempts were in all cases unsuccessful. A short account of them is appended.

**Triphenylmethylhydrazine Hydrochloride**,  $(\text{C}_6\text{H}_5)_3\text{C}-\text{NH}-\text{NH}_2\text{HCl}$ .—The preparation of this compound has already been described.<sup>1</sup> Some of the substance (0.5 g.) was triturated with anhydrous zinc chloride (3 g.) and the mixture heated in a test tube to  $300^\circ$ . No trace of aniline could be detected in the hydrolyzed reaction product.

**Benzophenonehydrazone**,  $(\text{C}_6\text{H}_5)_2\text{C}=\text{NNH}_2$ .—The substance was prepared according to Curtius.<sup>2</sup> The sample used melted at  $96.5^\circ$ . A small portion was heated for half an hour at  $100^\circ$  with an excess of concentrated sulfuric acid. No aniline or aniline sulfonate could be detected in the reaction product.

**Benzophenonehydrazone Hydrochloride**,  $(\text{C}_6\text{H}_5)_2\text{C}=\text{NNH}_2\text{HCl}$ .—The substance was prepared according to Curtius.<sup>3</sup> The sample used melted at  $182.5^\circ$ . One gram of substance was heated to  $275^\circ$  for ten minutes in a stream of dry hydrogen chloride. No aniline could be detected in the reaction product.

**Benzophenonephenylhydrazone**,  $(\text{C}_6\text{H}_5)_2\text{C}=\text{NNH}(\text{C}_6\text{H}_5)$ .—The substance was prepared according to Pickel.<sup>4</sup> The sample used melted at  $136.5^\circ$ . Some of the substance (2 g.) was heated for one hour at  $100^\circ$  with 20 cc. of concentrated sulfuric acid. No trace of aniline could be found in the reaction product. When the substance was treated at room temperature with dry hydrochloric acid gas, it was observed to turn red and absorb two molecules of hydrochloric acid which were given off again when the addition product was heated in the air. No formation of aniline could be detected.

One phenyl hydrazine derivative, after treatment with zinc chloride, gave a test for aniline. But as this might have been formed from the original substance by some process other than intramolecular rearrangement, its presence was not considered significant.

**$\alpha$ -Triphenylmethyl- $\beta$ -phenylhydrazine**,  $(\text{C}_6\text{H}_5)_3\text{C}-\text{NHNH}(\text{C}_6\text{H}_5)$ .—The substance was prepared according to the method of Gomberg.<sup>5</sup> The sample used melted at  $130^\circ$ . Some of the compound (0.5 g.) was triturated with 3 grams of anhydrous zinc chloride and the mixture heated at  $300^\circ$ . The steam distillate of the hydrolyzed reaction product gave a purple color with hypochlorite. It is not known whether the aniline, the presence

<sup>1</sup> See the preceding article.

<sup>2</sup> Curtius and Rauterberg, *J. prakt. Chem.*, [2] 44, 194 (1891).

<sup>3</sup> Curtius and Rauterberg, *Loc. cit.*

<sup>4</sup> Pickel, *Am. Chem. J.*, 232, 228 (1886).

<sup>5</sup> Gomberg and Berger, *Ber.*, 36, 1089 (1903).

of which is thus indicated, is formed by intramolecular rearrangement or by some other method. Lack of time prevented further investigation of the subject for the present. Further and more exhaustive work along all the lines opened by the experiments tried in this preliminary investigation will be carried out in the Kent Chemical Laboratory.

CHICAGO, ILL.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF PRESIDENCY COLLEGE.]

# HALOGENATION. XIII. METHODS OF ESTIMATION OF SEMI-CARBAZIDE, SEMIOXAMAZIDE AND OXALYLHYDRAZIDE BY THEIR INTERACTIONS WITH HALOGENS AND HALOGEN OXYACIDS.

BY RASIK LAL DATTA AND JOGENDRA KUMAR CHOUDHURY.

Received February 28, 1916.

In a previous paper<sup>1</sup> one of us has given reactions for the volumetric estimation of semicarbazide, using potassium chlorate, bromate and iodate in the presence of strong hydrochloric acid as oxidizing agents. Since hydrochloric acid decomposes chlorate, bromate and iodate with the evolution of halogens, the reactions described are evidently due to free halogens only. Hence a systematic study of the reactions of semicarbazide with the potassium salt of halogen oxyacids with dilute sulfuric acid was undertaken. Furthermore, it was found that substances which are similar in constitution, as those containing a hydrazine group— $\text{NHNH}_2$ , also undergo decomposition when subjected to the action of the halogens and halogen oxyacids with the liberation of a constant volume of nitrogen.

When semicarbazide is treated with potassium bromate, iodate or periodate in conjunction with sulfuric acid, a quantity of nitrogen which is always three-fourths of the theoretical is liberated. Bromine water also gives the same amount of nitrogen. Chlorine, which cannot be obtained in suitable concentration, is not suitable for such reactions. Potassium chlorate and sulfuric acid do not cause evolution of nitrogen since semicarbazide hydrochloride is stable in the presence of chloric acid and is not decomposed by it. Hypobromite solutions decompose semicarbazide with quantitative evolution of nitrogen. These reactions could be used for the volumetric estimation of the compound, since a constant quantity of nitrogen is always evolved under different conditions of dilution. Semioxamazide is also decomposed by the halogen oxyacids with the liberation of three-fourths of its nitrogen. With bromine, as also with hypobromite, quantitative liberation of nitrogen is the result. Oxalylhydrazide is decomposed by potassium bromate, iodate or periodate in conjunction with sulfuric acid as also by bromine water and hypobromite with the evolution of nitrogen, carbon dioxide and carbon monoxide. The evolu-

<sup>1</sup> Datta, *THIS JOURNAL*, 36, 1014 (1914).



tion of nitrogen is quite quantitative under varying conditions. Thiosemicarbazide is decomposed by the above reagents with the evolution of nitrogen, but the results obtained are quite anomalous and could not be used for the volumetric estimation of this substance. Aminoguanidine is decomposed by the reagents with the evolution of nitrogen, but the results obtained are quite varying. In the case of semicarbazide and semioxamazide the portion of nitrogen not evolved remains behind as ammonia, as has been noticed in a previous communication.<sup>1</sup> It was further confirmed as follows: Semicarbazide hydrochloride was treated with silver chlorate to form semicarbazide chlorate in solution. This decomposes with evolution of nitrogen on heating or evaporating, leaving behind pure ammonium chloride. A similar result was also obtained by evaporating a little semicarbazide hydrochloride with excess of bromine water, when ammonium bromide is left behind.

**Formation of Semicarbazide Chlorate.**—An interesting fact has been found in this connection. If the solution of semicarbazide chlorate prepared by double decomposition, instead of heating on the water bath, be allowed to evaporate in a vacuum desiccator, the chlorate is formed, which as soon as it assumes a solid state, decomposes with explosive violence. Quantities of less than a gram have been found to smash large vacuum desiccators to small pieces. As its isolation in a sufficiently cold atmosphere would entail much danger, it was not attempted.

**Formation of Urea from Semicarbazide.**—In this connection the isolation of semicarbazide nitrite was attempted by the double decomposition between semicarbazide hydrochloride and silver nitrite. The interaction is attended with effervescence, evidently due to the decomposition of the nitrite. On evaporating the filtrate, a solid was obtained which has been found to be pure urea melting at 132°. The yield of urea is quantitative, as the reaction is not accompanied by any secondary action.

**Estimation of Semicarbazide.**—Semicarbazide interacts with potassium bromate, iodate or periodate in the presence of sulfuric acid with evolution of three-fourths of the total nitrogen. With bromine water the same decomposition takes place. With chlorine water, however, the proper concentration could not be secured and hence this could not be used as a reagent for effecting the volumetric estimation of semicarbazide. Potassium chlorate and perchlorate do not decompose semicarbazide and hence they could not be used for the estimation of this compound.

The details for carrying out the experiments are as follows: A known weight of semicarbazide hydrochloride is dissolved in a known volume of water in a graduated test tube. One or two cc. of this solution is taken out in a pipet and poured down a Crum's nitrometer filled with mercury and then washed down with a little dilute sulfuric acid. Next, the finely

<sup>1</sup> *Loc. cit.*

powdered oxidizing agent, in excess to what is required for complete decomposition, is washed down with dilute sulfuric acid. As soon as the oxidizing agent is introduced there is a brisk evolution of gas which collects in the nitrometer. After a while the nitrometer is thoroughly shaken to ensure that the reaction is complete, when the solution becomes clear and does not effervesce. The gas which collects consists of a mixture of nitrogen and carbon dioxide. To remove the latter gas, the resulting mixture is washed thoroughly with water and then with caustic alkali when all the carbon dioxide is absorbed. The apparatus containing the gas is then removed to a cylinder full of water where the volume of the gas is read.

The results of the experiments with different reagents at varied concentrations are given below.

I.—WITH POTASSIUM IODATE AND SULFURIC ACID.

	Strength of the acid.	Strength of sol.	Vol. of sol. taken.	Vol. of N <sub>2</sub> .	Mean vol. of N <sub>2</sub> per cc.	Percentage of N <sub>2</sub> (theory for $\frac{1}{4}$ = 28.26%).
1.....	10%	0.2039 g. in 15 cc.	1 cc.	3.55		
			2 cc.	7.0	3.55	27.88
			1 cc.	3.6		
2.....	10%	0.1633 g. in 15 cc.	1 cc.	2.9	2.85	28.14
			2 cc.	5.6		
3.....	20%	0.2982 g. in 16 cc.	1 cc.	4.85		
			1 cc.	4.88	4.85	28.12
			1 cc.	4.82		
			1 cc.	4.85		
4.....	20%	0.1807 g. in 25 cc.	1 cc.	2.0		
			2 cc.	3.78	1.90	28.46
			2 cc.	3.70		
5.....	20%	0.1114 g. in 30 cc.	2 cc.	2.05		
			2 cc.	2.0	1.007	28.55
			2 cc.	2.0		

II.—WITH BROMINE WATER.

Found: 27.89; 27.99; 28.19; 28.21

III.—WITH POTASSIUM BROMATE AND SULFURIC ACID.

Found: 28.1; 28.34; 28.47; 28.5; 27.95

IV.—WITH PERIODATE AND SULFURIC ACID.

Found: 28.04; 28.57; 28.35

**Semioxamazide.**—Semioxamazide has a hydrazine group linked to a carbonyl group, as in the case of semicarbazide. It was therefore expected that it would decompose like semicarbazide and this has been found to be the case.

Semioxamazide is decomposed by potassium bromate, iodate or periodate in conjunction with sulfuric acid with evolution of three-fourths of the total nitrogen. With bromine water, however, quantitative liberation of nitrogen is the result. With hypobromite, the whole amount of ni-

trogen is evolved. Potassium chlorate and dilute sulfuric acid do not decompose this substance.

The experimental procedure is practically the same as in the case of semicarbazide. Semioxamazide, however, is but sparingly soluble in water, hence a solution of it is prepared in dilute sulfuric acid which has no action on it. As the gas obtained contains carbon dioxide, it is always washed with a solution of caustic potash. The conditions of experiments are varied a good deal as with semicarbazide, *viz.*, using sulfuric acid of different dilution, as also varying strength of semicarbazide solution or using varying excesses of the oxidizing agent. But in all cases the evolution of gas is quite constant. With bromine water the gas does not evolve as soon as it comes in contact with the solution. On shaking, however, nitrogen begins to collect rapidly. The results of experiments are given below.

I.—WITH POTASSIUM PERIODATE AND SULFURIC ACID.

Found: 30.51; 30.25; 30.45; 30.65. Theory ( $\frac{3}{4}$ ) 30.6

II.—WITH POTASSIUM IODATE AND SULFURIC ACID.

Found: 30.57; 30.37; 30.67; 30.47

III.—WITH POTASSIUM BROMATE AND SULFURIC ACID.

Found: 30.75; 30.44; 30.39; 30.71

IV.—WITH BROMINE WATER.

Found: 40.69; 40.52; 40.47; 40.67. Theory (total), 40.8

V.—WITH SODIUM HYPOBROMITE.

Found: 40.59; 40.67; 40.82

**Oxalylhydrazide.**—Oxalylhydrazide decomposes in the presence of oxidizing agents giving one molecule of carbon dioxide, one molecule of carbon monoxide and two of nitrogen according to the equation



After the absorption of carbon dioxide by alkali and carbon monoxide by ammoniacal cuprous chloride, it has been found that the volume of nitrogen is quite constant and hence the reactions can be used as a method for the volumetric estimation of the compound. As the substance is not soluble in the ordinary solvents, use was made of the slight solubility of the substance in water acidulated with a little sulfuric.

The results of experiments are given below.

I.—WITH POTASSIUM IODATE AND SULFURIC ACID.

Found: 47.65; 47.36; 48.59. Theory (total), 47.45

II.—WITH POTASSIUM PERIODATE AND SULFURIC ACID.

Found: 47.21; 47.31; 47.66

III.—WITH POTASSIUM BROMATE AND SULFURIC ACID.

Found: 47.51; 47.39; 47.88

IV.—WITH BROMINE WATER.

Found: 47.15; 47.59; 47.51

V.—WITH SODIUM HYPOBROMITE.

Found: 47.22; 47.83; 47.66

Investigations on similar lines are being continued.

CALCUTTA, INDIA.

[FROM THE RESEARCH LABORATORY OF PARKE, DAVIS &amp; COMPANY.]

## STUDIES ON DERIVATIVES OF TRIHALOGENTERTIARY-BUTYL-ALCOHOLS.

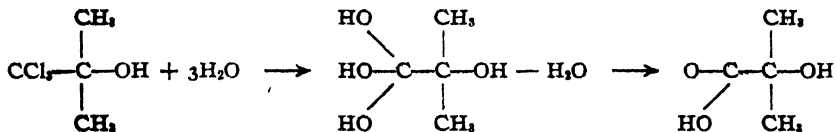
## I. THE ACETIC ESTER OF TRIBROMOTERTIARY-BUTYL-ALCOHOL OR BROMETONE ACETIC ESTER.

BY T. B. ALDRICH AND C. P. BECKWITH.

Received September 27, 1916.

The trichloro- and tribromotertiary-butyl-alcohols are most interesting compounds, both chemically and pharmacologically. The trichloro-compound, "Chloretone,"<sup>1</sup> has pronounced hypnotic, sedative and anesthetic properties, both local and general, and the same may be said of the tribromo-compound, "Brometone,"<sup>2</sup> which is considered to have more marked sedative, but less pronounced hypnotic and anesthetic properties. Both compounds are sparingly soluble in water (chloretone 0.8% and brometone still less), but readily soluble in the organic solvents; both have a camphor-like odor and taste, are readily volatile in the air or with steam, and may be crystallized from dilute alcohol and obtained in the form of beautiful white crystals. Both compounds combine with water more or less firmly and in this respect resemble chloral, although the water is not chemically bound as in the latter substance to form a stable hydrate.

The three halogens attached to one carbon atom impart to these bodies properties different from those of the unsubstituted tertiary alcohols; indeed, as pointed out by Willgerodt,<sup>3</sup> they may be regarded as trihalides of  $\alpha$ -hydroxyisobutyric acid, for they yield  $\alpha$ -hydroxyisobutyric acid upon treatment with alkalis under suitable conditions, probably thus:



The trichlorotertiary-butyl-alcohol may be crystallized from warm moderately concentrated nitric acid without material decomposition. With care the tribromo-alcohol may be similarly crystallized, though with considerable decomposition. They are broken down by concentrated sulfuric acid and by moderately dilute caustic alkali solutions(5%). In general, they are chemically rather inert bodies, fairly resistant to anything

<sup>1</sup> Chloretone and <sup>2</sup>brometone are the commercial names given the trichloro- and tribromotertiary-butyl-alcohols, respectively.

<sup>3</sup> Ber., 15, 2305 (1882).

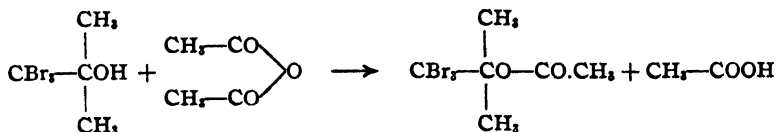
short of destructive treatment. Willgerodt was unable to replace the chlorine of chloretone by alkyls.<sup>1</sup> It is interesting to note, however, that they form readily a series of esters of remarkable properties, and it is principally with these esters and related compounds that we are concerned in these articles.

It may be well to say in anticipation that one of the most striking properties of this series of esters is their relatively great stability—a fact that was noted by one of us (C. P. B.) in 1903. At that time the salicyclic ester of trichlorotertiary-butyl-alcohol was prepared and studied chemically and pharmacologically in the hope that it might be found to possess therapeutic value comparable with that of salol. The substance proved to be quite resistant to more or less heroic chemical treatment and to pass through the alimentary tract unchanged. Pharmacologically and clinically it appeared to be almost, if not quite, inert. These findings were not published at the time and later the compound was produced in Germany and patented.<sup>2</sup>

An observation very useful in the purification of these esters is that all of them, so far prepared by us, seem to be quite unaffected by gentle warming with caustic alkali solutions of 5–10%, while the uncombined alcohols themselves are broken down and readily removed by this treatment.

In a former article one of us<sup>3</sup> obtained by acetylating trichlorotertiary-butyl-alcohol with acetic anhydride and anhydrous sodium acetate in the usual manner, an ester to which the name acetyl chloretone was given. It has since been noted that this ester had already been prepared and briefly described by Willgerodt<sup>4</sup> under the unusual name, however, of acetyl-oxy-isobutyric-acid-trichloride.

The present article is concerned chiefly with the preparation and properties of a like compound of tribromotertiary-butyl-alcohol, the brometone acetic ester being formed similarly to the chloretone ester according to the following equation:



**Preparation.**—(a) One part of brometone is boiled with two parts of acetic anhydride and one part of anhydrous sodium acetate for two hours, using a reflux condenser. During the heating, the mixture becomes slightly colored, due, no doubt, to the splitting off of bromine or bromine

<sup>1</sup> *J. prakt. Chem.*, **39**, 283–289 (1889).

<sup>2</sup> R. Wolfenstein, D. R. P. No. 267,381.

<sup>3</sup> T. B. A., *THIS JOURNAL*, **37**, 2720 (1915).

<sup>4</sup> *J. prakt. Chem.*, **39**, 283–289 (1889).

compounds. On cooling, the mixture solidifies and on adding water and allowing to stand for some time two layers form, the upper being water, acid, sodium acetate, etc., the lower containing the product desired.

The upper layer is decanted as closely as possible, the residue warmed gently with an excess of caustic soda solution, and after standing some time extracted with ether. The ethereal extract is washed thoroughly, then filtered and the ether allowed to evaporate. The residue left is distilled with steam. A colorless oil passes over, having an odor very similar to, but not so pronounced as that of chloretone acetic ester. It is collected with ether, filtered, and the ether allowed to evaporate. Yield of nearly 50%. It colored slightly yellow on standing, and solidified. When purified by recrystallizing from alcohol it is white and melts at 43-44° (uncorr.).

(b) The following method of preparation is simpler and gives nearly a quantitative yield:

Dissolve two parts of brometone in four parts of glacial acetic acid and to this solution add one and a half parts of acetyl bromide or one part of the chloride. The mixture becomes warm and fumes of the halogen acid are given off. After the reaction has proceeded at room temperature for some time, the flask is heated on the steam bath for two hours and then allowed to stand overnight. Dilute caustic alkali is then added and the mixture warmed to decompose any excess of acetyl haloid or brometone. The ester settles then to the bottom of the vessel as an oil. The water etc., above the oil is decanted and the latter washed several times with water. This oil on cooling strongly, and especially when inoculated with a crystal of the ester, solidifies at once in crystalline form. It may be recrystallized from alcohol. The yield is nearly quantitative.

The preparation may also be carried out without the use of glacial acetic acid as a diluent. In this case the acetyl haloid is poured directly on the brometone, but considerable heat is evolved and it is advisable to provide for adequate cooling. After the reaction is ended, the vessel is heated on the steam bath until very little acid is given off. The compound is then treated as in the other cases.

Whichever method is used, economy of acetylating reagents is served, no doubt, by preliminary drying of the brometone as far as practicable. On the other hand, attempts to dry brometone thoroughly by most of the usual methods entail loss of this substance through volatilization, decomposition, or otherwise. For use in the reaction under discussion, a few days' standing in a desiccator over calcium chloride will suffice. (Sulfuric acid should not be used as a drying agent, since it absorbs and decomposes brometone vapor.) In fact, save that a larger proportion of the acetylating reagent is required, there is no objection to using ordinary crystallized brometone without preliminary drying.

Bromine determinations (Carius) carried out with a product recrystallized several times from moderately strong alcohol and melting at 43–44°, gave the following results:

0.4672, 0.2869, 0.2697, and 0.2584 g. gave 0.3161, 0.1985, 0.1841, and 0.1775 g. Br. Calc. for  $C_6H_5O_2Br_3$ : 67.99% Br. Found: 67.66, 69.20, 68.26, and 68.69%.

Leaving out the second value the results are sufficiently near, especially when the method of preparation is considered, to characterize the compound, without the necessity of making a combustion analysis, as the brometone acetic ester.

**Properties.**—The compound is extremely soluble in strong alcohol, acetone, chloroform, ether, glacial acetic acid, benzene, etc., insoluble in water. The alcoholic solution is precipitated by water.

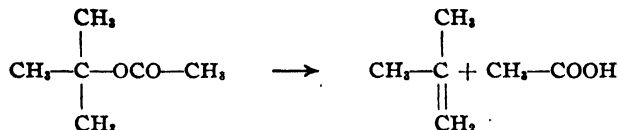
When boiled with water for some time (29 hrs.), using a reflux condenser, a portion of the substance in the form of an oil, estimated at 0.5 of that taken originally, is found undecomposed. This oil on cooling has a tendency to crystallize. The supernatant liquid is strongly acid toward litmus and gives a heavy yellowish precipitate with  $AgNO_3$ , soluble, though not quickly in an excess of strong ammonia. There is no evidence of the alcohol in the condenser, as was the case when the chloretone ester was treated similarly. No brometone or other body is thrown out by diluting the supernatant liquid with water. Further boiling for 21 hours completely decomposes the remainder of the oil. Probably the brometone ester is saponified and then the brometone decomposed. When brometone acetic ester is boiled with water, to which  $H_2SO_4$  has been added, decomposition takes place in about the same time as when water alone is used.

Three grams of the substance were placed in a pressure tube with 10 cc. of  $H_2O$  and heated for three hours at 160°. There was a slight pressure on opening the tube, a combustible gas was given off, and an oil insoluble in  $H_2O$  had formed which did not solidify on cooling in ice water. On reheating the resealed tube for several hours at 170° complete decomposition of the oil-like substance had taken place, the homogeneous liquid had become yellowish, had a strong acid reaction toward litmus and showed the presence of large quantities of hydrobromic acid and of traces of acetic acid. By diluting with water, brometone was not thrown out. Partial carbonization had occurred.

Although saponification takes place slowly by boiling with water or water and dilute sulfuric acid, it takes place very rapidly when the ester is heated with an excess (three or four times its volume) of concentrated nitric acid. In fact, the brometone ester conducts itself in general toward hot nitric acid the same as the chloretone ester, except that the brometone which is produced at first readily undergoes further decomposition if heat is applied too long. In saponifying the brometone ester the procedure is as follows: Heat with the acid over a free flame until the ester

dissolves. Then cool under running water. If a cloudiness appears, the saponification is not far enough advanced. Heat gently until on cooling the solution remains clear, then dilute with an excess of water. The brometone is precipitated and may be recrystallized from dilute alcohol.

Here again, as with chloretone acetic ester, it is to be noted that saponification may occur with reproduction of the original acid and alcohol, while the usual rule with tertiary alcohols is that an unsaturated hydrocarbon appears instead of the alcohol, thus:



Brometone acetic ester volatilizes slowly, much more slowly than brometone. Placed on a watch glass under a funnel at summer temperature for 12 days, it lost 23% of its weight. In the incubator for 7 days a sample lost 12.5%. Under like conditions the loss of brometone is much greater.

The following preliminary data relative to the pharmacological action of brometone acetic ester as compared with chloretone were kindly furnished by our associate, Mr. L. W. Rowe:

"The toxicity of this preparation was determined by intraperitoneal injection into guinea pigs of an olive oil solution and the minimum fatal dose was found to be 0.5 g. per kg. body weight, that of chloretone being 0.15 g. per kg. body weight.

Because of the practically complete insolubility of the product in water, it was impossible to determine the irritation, if any, which was produced by hypodermic injection. When an olive oil solution was used, some irritation was produced after some hours due to the very slow absorption. When a strongly alcoholic solution was used, irritation was produced immediately by the alcohol. The product itself probably does not possess very irritating properties.

Concerning the anesthetic and sedative action of this drug we can say that as the dose approaches very near the toxic dose, an anesthetic action is observed several hours after administration. The slow action is no doubt due to the very slow absorption of the drug. The anesthetic action, which may be partially due to the toxicity of the drug, is certainly not as strong or as rapidly evidenced as that produced by chloretone.

The action of brometone acetic ester upon the laid-bare frog's heart is not as strong as is that of chloretone.

The blood pressure of an anesthetized dog was somewhat lowered after the intravenous injection of rather large amounts of this drug (4 cc. of a 2% solution in 50% alcohol). A control injection of the same amount of alcohol alone failed to produce as marked a reaction.



In summarizing these data it seems that brometone acetic ester is somewhat similar to chloretone in its pharmacological action but that the action of the former is not nearly as strong or as quickly evidenced. The latter fact can partially be accounted for by the extreme insolubility in water of the brometone acetic ester."

Further pharmacological studies are being made with these esters in comparison with chloretone and brometone.

Owing to delay and confusion in the mails from Germany, there has just reached us an article by R. Wolffenstein, A. Loewy and M. Bachstez on "Esters of Trichlorotertiary-butyl-alcohol and Their Pharmacology."<sup>1</sup> The details of their pharmacological findings are published in a separate article in a number of Schmiedeberg's Archiv. that has not yet come to hand. For the present, it will suffice to say that the results obtained by these gentlemen with the chloretone esters are, in most points, quite in accord with ours with the brometone esters in so far as we have followed parallel lines.

According to these authors the preparation of the esters is ordinarily easily carried out through the action of the acid chloride with or without the aid of tertiary bases, in fact from the acid and the alcohol in the presence of a condensing agent.

The following facts were observed by Wolffenstein relative to the esters of trichlorotertiary-butyl-alcohol: They are not as a rule split up in the body; they exhibit an unexpected action quite different from that of the alcohol from which they are prepared; and they exhibit poisonous properties, causing cramps. These cramps or convulsions begin to manifest themselves in chloretone acetic ester, increasing in the higher homologues and reaching the maximum as far as investigated in the ester of isovaleric acid.

It is further stated that the chloretone acetic ester, the one most thoroughly studied, shows less narcotic action but greater poisonous properties than chloretone.<sup>2</sup> The decrease in narcotic property and increase in poisonous property is shown much more plainly in the propionic ester and still more in the isovaleric ester. The isovaleric ester has no hypnotic action, but has, at least on rabbits, a toxic action causing convulsions.

The authors furthermore state that the only<sup>3</sup> known ester of trichlorotertiary-butyl-alcohol, up until the appearance of their article, is the

<sup>1</sup> *Ber.*, 48, 2035-43 (1916).

<sup>2</sup> According to the results of Aldrich relative to the toxicity of acetyl-chloretone (trichlorotertiary-butyl acetic ester) it was found (*THIS JOURNAL*, 37, 2722 (1915)) that "The toxicity of this acetyl-ester, when introduced subcutaneously into guinea pigs, is slightly less than that of Chloretone." Possibly Wolffenstein and his collaborators employed another method of administration, which would account for the different findings.

<sup>3</sup> Willgerodt prepared also the benzoic ester, *J. prakt. Chem.*, *loc. cit.*

acetic acid ester prepared first by Willgerodt under the name acetyl-oxy-isobuttersäure-trichloride. [Later by Aldrich under the name mono-acetyl trichlorotertiary-butyl-alcohol (chloretone acetic ester).]

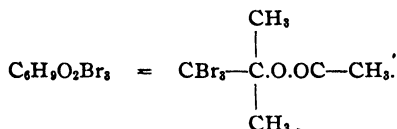
The following esters of chloretone were prepared by Wolfenstein: Propionic ester (yellow oil); isovaleric ester (oil); bromoisovaleric ester (oil); monochloroacetic ester (cryst.); trichloroacetic ester (cryst.); diethyl glycine ester (oil); dimethyl glycine ester (oil); piperidine acetyl ester (cryst.); allophanic ester (cryst.); acid malonic ester (cryst.); dibromocinnamic ester (cryst.); neutral malonic ester (cryst.).

### Summary.

The acetic ester of tribromotertiary-butyl-alcohol is most conveniently prepared through the interaction of acetyl chloride or bromide and the alcohol, or by means of acetic anhydride and anhydrous sodium acetate, in the usual way.

Prepared by either of these processes and recrystallized from alcohol, the purified substance melts at 43-44° (uncorr.).

Bromine determinations (Carius) gave results sufficiently near to characterize the compound as brometone acetic ester with the formula



The compound is extremely soluble in the organic solvents, practically insoluble in water. It is not readily saponified by boiling with water or acidulated water and when saponified the alcohol is decomposed still further. Although saponification takes place slowly by boiling with water or water and acid, it takes place very quickly when heated with an excess of moderately concentrated nitric acid. Like chloretone and brometone, though not quite so readily, the ester is volatile in the air and especially with steam. The pharmacological action is similar to that of chloretone and brometone although, presumably on account of its greater insolubility in water, its effects are less rapid and marked.

DETROIT, MICH.

[CONTRIBUTION FROM CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY.]

### STUDIES IN ESTERIFICATION. VII.

#### THE ESTERIFICATION OF *o*-, *m*- AND *p*-TOLUIC ACIDS BY ETHYL MERCAPTAN.

By J. H. SACHS AND E. EMMET REID.

Received September 27, 1916.

#### Historical.

As early as 1862 Berthelot and Pean de St. Gilles<sup>1</sup> began the investigation of the general problem of esterification. They studied the limit of

<sup>1</sup> *Ann. chim. phys.*, [3] 65, 385 (1862); 66, 5 (1862); 68, 225 (1863).

esterification for different temperatures. In 1878 Menshutkin<sup>1</sup> took up the problem and by using different alcohols with acetic acid first showed the effect of composition and isomerism on the rate and limit of esterification. Goldschmidt<sup>2</sup>, in 1895, first studied the effect of differences of constitution in isomeric acids upon ester formation. He studied the esterification of *o*-, *m*- and *p*-substituted benzoic acids with ethyl alcohol, using hydrochloric acid as catalyzer. By using a large excess of alcohol in which the hydrochloric acid was dissolved, he was able to use for the calculation of his results the equation for a monomolecular reaction:

$$K = (1/t) \log a/a - x$$

For the toluic acids he got the following constants:

<i>o</i> -Toluic.....	0.011
<i>m</i> -Toluic.....	0.0470
<i>p</i> -Toluic.....	0.0241

The same general relation was noted for other substituted benzoic acids.

About the same time Petersen<sup>3</sup> observed that *p*-toluic acid forms ester much more readily than does the ortho acid.

From 1894 to 1897 Victor Meyer<sup>4</sup> and his co-workers, investigating the problem of steric hindrance, threw much light on the effect of isomerism upon esterification. Working with ethyl and methyl alcohols with ortho, meta and para substituted benzoic acids, they showed that the toluic acids were esterified in the following order: Meta, para and ortho. The same held good for other monosubstituted benzoic acids.

Kellas<sup>5</sup> extended the work of Victor Meyer and found practically the same results. He also studied the rate of saponification of esters of the substituted benzoic acids by caustic potash. In the case of the esters of the toluic acids the results are so close together that no general relation can be gotten from them.

Recently McCombie and Scarborough<sup>6</sup> in studying the rate of saponification of esters of substituted benzoic acids by hydrochloric acid, found the following constants:

	<i>o</i> .	<i>m</i> .	<i>p</i> .
Toluic.....	0.00134	0.00405	0.00275
Chlorobenzoic.....	0.0158	0.0485	0.0298
Bromobenzoic.....	0.0118	0.0445	0.0234

Thus we see that the saponification relation is the same as that of esterification.

<sup>1</sup> *Ann.*, **195**, 334 (1878).

<sup>2</sup> *Ber.*, **18**, 3218 (1895).

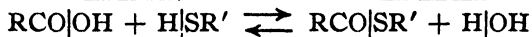
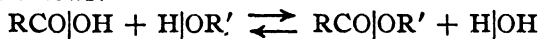
<sup>3</sup> *Z. physik. Chem.*, **16**, 403 (1895).

<sup>4</sup> *Ber.*, **27**, 510, 3146 (1894); **28**, 1254, 2773, 3197 (1895); *Z. physik. Chem.*, **24**, 219 (1897).

<sup>5</sup> *Z. physik. Chem.*, **24**, 221 (1897).

<sup>6</sup> *J. Chem. Soc.*, **107**, 156 (1915).

Reid<sup>1</sup> in studying the mechanism of the reaction in esterification showed that mercaptans esterify acids just as do alcohols. However, instead of getting esters of the general formula  $\text{RCOOR}'$ , he got the thiol esters of the general formula  $\text{RCOSR}'$ . This shows that esterification probably takes place as follows:



The present work was taken up therefore with the idea of finding whether or not the above relations hold when the toluic acids are esterified with ethyl mercaptan.

### Materials.

**Acids.**—The *o*- and *m*-toluic acids were a well-known firm's best grade. The *p*-toluic acid was made from *p*-tolyl nitrile which, in turn, was made from *p*-toluidine by the Sandmeyer reaction. This acid was purified by boiling with animal charcoal and then twice recrystallizing from boiling water, m. p. 177°.

**Mercaptan.**—The ethyl mercaptan was made by Reid for use in the above-mentioned work. It had been freed from sulfide, dried, and twice distilled, only the best fraction being used for the work.

The thiol esters were made by alkylating the thiol toluic acids which were prepared according to the directions of Kym<sup>2</sup> for thiolbenzoic acid.

***o*-Thiol Toluic Acid.**—To 80 g. of 85% caustic potash dissolved in 600 cc. of 95% alcohol and saturated with hydrogen sulfide, there was added, with cooling, 70 g. of *o*-toluyl chloride. The potassium salt of the *o*-thiol acid separated at once as a pasty brown mass. This was dried on the water bath, taken up with water and the solution shaken with ether in order to remove any ethyl toluate that might have been present. On acidifying the water solution of the potassium salt with hydrochloric acid, the acid separated as a red oil. This was taken up with ether, the ethereal solution dried over calcium chloride and, after distilling off the ether, the ester was twice distilled *in vacuo*. The yield was 26 g.; b. p. 133°<sup>35</sup>; d. 1.145<sub>125</sub><sup>25</sup>. Weighed portions of the acid were dissolved in alcohol and titrated with 0.0905 *N* barium hydroxide.

I. 0.1559 g. acid required 11.32 cc. alkali; corresponding to M. W. 152.18.

II. 0.1418 g. acid required 10.62 cc. alkali; corresponding to M. W. 152.71.

Calculated, M. W. 152.12.

***p*-Thiol Toluic Acid.**—This was made in exactly the same way as the preceding. The acid separated as a red oil which on cooling, solidified. The yield was 48 g. from 70 g. of *p*-toluyl chloride. B. p. 131°<sup>15</sup>. M. p. after recrystallizing from alcohol 43.5–44°. This was also titrated with the standard alkali.

<sup>1</sup> *Am. Chem. J.*, 43, 489 (1910).

<sup>2</sup> *Ber.*, 32, 3533 (1899).

I. 0.1409 g. acid required 10.30 cc. alkali; corresponding to M. W. 152.64.

II. 0.1981 g. acid required 14.44 cc. alkali; corresponding to M. W. 152.38.

The *m*-thiol toluic acid and its ethyl ester could not be made on account of the scarcity of *m*-xylene and *m*-toluidine.

**Ethyl *o*-Thiol Toluatoe.**—This was made by Wheeler's method for ethyl thiol benzoate, from potassium *o*-thiol toluate and ethyl bromide. The yield was 25 g. from 30 g. of the acid and 35 g. of ethyl bromide. B. p. 133<sup>015</sup>. D. 1.0513<sup>25</sup><sub>25</sub>. The ester has a clear yellow color which has remained unchanged after standing five months.

**Ethyl *p*-Thiol Toluatoe.**—This was made exactly as was the ortho ester. From 25 g. of the acid and 30 g. of ethyl bromide 23 g. of the ester were obtained. B. p. 150<sup>018</sup>. D. 1.0708<sup>25</sup><sub>25</sub>. This ester has also remained unchanged on five months' standing.

All of these acids and esters are insoluble in water, but dissolve readily in alcohol and ether. They are very resistant to oxidation by nitric acid, for after heating them five hours in a Carius tube with fuming nitric acid at 250°, they were not burned up.

The authors have been working for some time upon a new method for the determination of sulfur in organic compounds. The analysis of these acids and esters will appear in a later paper upon this method.

**Water.**—Conductivity water was used.

#### Heating.

The furnace used was that described by Pratt and Reid;<sup>2</sup> electrically controlled and heated, it maintained the desired temperature for weeks with a variation of  $\pm 2^\circ$ .

#### Standard Solution.

The standard hydrochloric acid and barium hydroxide were kept in large stock bottles from which they were run through siphons fitted with stopcocks into their respective burets. The tops of the acid bottle and buret were protected from the air by tubes containing acid of the same strength as the standard solution. The barium hydroxide system was protected by soda lime tubes. Both solutions were approximately 0.1 *N* and were frequently standardized.

#### Procedure.

Hard glass tubes about 6 by 70 mm. outside, closed at one end, were cleaned by boiling one day in dilute hydrochloric acid, 4 hours in distilled water and then thoroughly dried in an air bath at 150°.

**Acid Series.**—Each tube was weighed, partly filled with the acid, drawn out to a narrow neck and weighed again. The mercaptan was then added and after cooling in ice and salt, the tubes were sealed. The tube and tip were then weighed.

<sup>1</sup> *Am. Chem. J.*, 24, 69 (1900).

<sup>2</sup> *THIS JOURNAL*, 37, 1934 (1915).

**Ester Series.**—The procedure was the same as for the acid series, using ester instead of acid, and water instead of mercaptan.

These tubes were then placed in the furnace and heated to 198–202° for different periods of time. On taking the tubes from the furnace they were allowed to cool, scored with a file and broken over a short necked funnel into 120 cc. Erlenmeyer flasks. The funnel was rinsed with 25 cc. of ethyl alcohol, which had been distilled from caustic potash, which dissolved the reaction mixture. The mercaptan which had not reacted, was blown off by bubbling for 15 minutes through the solution, kept at 50°, a current of carbon dioxide-free air. The amount of toluic acid present was then determined by titration with the standard baryta water, using phenolphthalein as indicator. Uniformity of results was gotten by standardizing the baryta with alcoholic solutions of the toluic acids used.

### Experimental.

The chief object of the work was to measure the limits of esterification, but the rates also are of interest. The velocities of esterification are calculated by the formula for bimolecular reactions:<sup>1</sup>

$$(1) \quad K = \frac{2.3025}{(A - B)T} \log \frac{(A - x)B}{(B - x)A}$$

in which A and B are the active masses of the two substances that react, x the amount of each transformed and T the time. As this equation holds even approximately, for balanced reactions, only when the reaction is proceeding with an appreciable velocity, that is, before the limit is nearly reached, it was applied to only the one-, two- and four-day series.

The limits of esterification are gotten by the usual reasoning in consideration of reversible reactions.<sup>2</sup> In this case the amount of ester formed in unit time being equal to (Acid  $\times$  Mercaptan) K and the amount of ester decomposed at the same time being equal to (Ester  $\times$  Water) K', at equilibrium these velocities being equal, we have

$$(2) \quad \frac{(\text{Acid} \times \text{Mercaptan})}{(\text{Ester} \times \text{Water})} = \frac{K'}{K} = r.$$

For equal concentrations of acid and mercaptan at equilibrium,

$$\frac{\text{Amount of mixture unesterified}}{\text{Amount of mixture esterified}} = \frac{\sqrt{K'}}{\sqrt{K}} = \frac{\sqrt{r}}{1}$$

or, the percentage of a mixture of equivalent amounts, esterified at limit =  $100/\sqrt{r} + 1$ .

In the following tables are given the results of the *o*-, *m*-, and *p*-toluic acids with ethyl mercaptan and the results of the *o*-, and *p*-ethyl ester with water.

<sup>1</sup> Reid, *Am. Chem. J.*, **24**, 398 (1900).

<sup>2</sup> Reid, *Ibid.*, **43**, 499 (1910); Bonz, *Zeit. physik. Chem.*, **2**, 865 (1888).

In tabulating the results, the data are thus arranged.

- a*, Acid or ester in grams.
- b*, Millimols of acid or ester.
- c*, Mercaptan or water in grams.
- d*, Millimols of mercaptan or water.
- e*, Cubic centimeters of standard alkali required for titration.
- f*, Millimols of acid present, calculated from *e*.
- g*, Millimols of mercaptan remaining (acid series).
- h*, Millimols of ester remaining (ester series).
- k*, Millimols of water remaining (ester series).
- m*, Millimols of ester, equals water (acid series).
- %, Percentage of esterification, calculated by the above formula.
- x*, The same as *m* in acid series and *f* in ester series.
- K*, The velocity constant of the reaction.

In the acid series the amount of ester = water, (*m*) is found by subtracting the acid remaining (*f*) from the original amount (*b*). The concentration of ester (*m*) equals the concentration of water. The millimols of mercaptan remaining, as given in (*g*), are obtained by subtracting the amount of ester (*m*) from (*d*), the amount of mercaptan originally present.

In the ester series, the amount of ester remaining (*h*) is found by subtracting the acid present from (*b*), the original amount of ester. The water remaining (*h*) is obtained by subtracting the acid present (*f*) from (*d*), the original amount of water.

The percentage esterification (%) and the velocity constant of the reaction (*K*) are obtained by calculation from the equations above discussed. In Series I all the data are tabulated, but in the tables that follow only the most essential are given. Some of the results which are out of harmony with others of same series are bracketed and are not included in the averages.

The work was undertaken as a study of the limits rather than the reaction velocities. Hence close temperature regulation and other precautions required for obtaining concordant values of *K* were not regarded. The values of *K* are only approximate and little stress is put on them.

### Results.

#### SERIES I.—24 HOURS AT 200°.



<i>a</i>	0.0669	0.0935	0.0817	0.0774	0.0778	0.0910
<i>b</i>	0.4919	0.6875	0.6007	0.5691	0.5722	0.6691
<i>c</i>	0.1242	0.1206	0.1605	0.0941	0.1680	0.1095
<i>d</i>	2.001	1.9428	2.586	1.515	2.707	1.765
<i>e</i>	5.32	7.21	6.48	5.98	6.21	7.09
<i>f</i>	0.4816	0.6529	5.846	5.412	0.5625	6.419
<i>g</i>	1.991	1.9082	2.570	1.487	2.697	1.738

$m$	0.0103	0.0346	0.0161	0.0279	0.0097	0.0272
$\sqrt{r}$	95.07	32.26	76.13	32.15	127.9	38.83
%	1.04	3.01	1.30	3.02	0.78	2.51
K	0.0110	0.0267	0.0101	0.0338	0.00637	0.0235

Mean K, 0.0186.

Mean, 1.94%.



$a$	0.1104	0.1324	0.1412	0.1609	0.0468	0.0420	0.0410	0.0507	0.0479
$b$	0.8118	0.9735	1.0375	1.183	0.3441	0.3088	0.3015	0.3728	0.3522
$c$	0.1690	0.1705	0.1238	0.1091	0.2641	0.1813	0.1621	0.1271	0.0939
$d$	2.723	2.747	1.995	1.758	4.255	2.921	2.612	2.048	1.513
$e$	8.00	8.72	10.24	11.92	3.48	3.11	3.04	3.85	3.58
$f$	0.7240	0.7882	0.9267	1.079	0.3150	0.2815	0.2751	0.3484	0.3240
$g$	2.635	2.5616	1.884	1.654	4.230	2.894	2.586	2.024	1.485
$m$	0.0878	0.1854	0.1108	0.1040	0.0291	0.0273	0.0264	0.0244	0.0282
$\sqrt{r}$	15.73	7.66	11.93	12.85	39.67	33.06	31.95	34.42	24.60
%	5.98	(11.55)	7.73	7.22	2.46	2.94	3.04	2.83	3.91
K	0.0428	0.0697	0.0579	0.0541	0.0207	0.0316	0.0354	0.0331	0.0558

Mean K, 0.0516.

Mean, 6.98%.

Mean K, 0.0353.

Mean, 3.03%.



$a$	0.2846	0.2734	0.2601	0.2820	0.2875	0.2722
$b$	1.5807	1.5184	1.4447	1.5662	1.5968	1.5180
$c$	0.2891	0.2104	0.2003	0.1634	0.1357	0.1398
$d$	16.061	11.688	11.128	9.078	7.539	7.767
$e$	2.60	2.70	2.01	1.44	1.92	2.66
$f$	0.2353	0.2444	0.1819	0.1303	0.1738	0.2407
$h$	1.3454	1.2740	1.2628	1.4359	1.4230	1.2711
$k$	15.826	11.446	10.946	8.948	7.365	7.526
$\sqrt{r}$	0.0510	0.0640	0.0489	0.0364	0.0537	0.0778
%	95.18	93.98	95.32	96.50	94.90	(92.80)
K	0.0102	0.0153	0.0125	0.0126	0.0154	(0.0229)

Mean K, 0.0132.

Mean, 95.17%.



$a$	0.2947	0.2551	0.2487	0.2682	0.2544	0.2663
$b$	1.6367	1.4168	1.3813	1.4897	1.4129	1.4790
$c$	0.1411	0.1747	0.1307	0.1862	0.1594	0.1844
$d$	7.8390	9.7055	7.2610	10.3440	8.8555	10.2440
$e$	8.55	5.95	3.86	5.95	8.08	8.14
$f$	0.7738	0.5385	0.3493	0.5385	0.7312	0.7367
$h$	0.8629	0.8783	1.0320	0.9512	0.6817	0.7423
$k$	7.0652	9.1670	6.9117	9.8055	8.1243	9.5073
$\sqrt{r}$	0.3134	0.1898	0.1308	0.1763	0.3106	0.2774
%	76.17	84.05	88.40	85.10	76.30	78.25
K	0.0860	0.0512	0.0409	0.0446	0.0864	0.0712

Mean K, 0.0634.

Mean, 81.21%.



## SERIES II.—48 HOURS AT 200°.



<i>b</i>	1.0405	1.089	0.9500	0.7522	0.7647
<i>d</i>	3.0285	3.5804	3.9108	1.281	3.2760
<i>f</i>	0.9957	1.0300	0.8960	0.7023	0.7321
$\sqrt{r}$	35.91	32.28	34.43	18.60	47.27
%	2.71	3.00	2.83	(5.10)	2.08
K	0.00736	0.00819	0.00742	(0.0280)	0.00451

Mean K, 0.00687. Mean, 2.65%.



<i>b</i>	1.5883	1.0118	1.1831	0.9721	0.4059	0.6559	0.4956	0.5780
<i>d</i>	1.9578	2.3623	2.1544	1.3954	2.8875	5.2788	2.5507	2.8715
<i>f</i>	1.4426	0.8823	1.0208	0.8751	0.3701	0.5819	0.4317	0.5294
$\sqrt{r}$	11.10	10.84	8.79	10.99	28.70	23.51	16.22	25.16
%	8.26	8.63	10.23	8.34	3.37	4.08	5.81	3.82
K	0.0249	0.0298	0.0343	0.0302	0.0164	0.0114	0.0266	0.0153

Mean K, 0.0298.

Mean, 8.81%.

Mean K, 0.0174.

Mean, 4.27%.



<i>b</i>	1.3684	1.5545	1.5507	1.6034	1.6451
<i>d</i>	8.4778	16.061	11.406	12.917	14.067
<i>f</i>	0.1376	0.2742	0.3493	0.3321	0.2471
$\sqrt{r}$	0.0429	0.0610	0.0958	0.0830	0.0562
%	95.9	94.2	91.3	92.4	94.7
K	0.00627	0.00608	0.0113	0.00890	0.00585

Mean K, 0.00768. Mean, 93.7%.



<i>b</i>	1.5579	1.4518	1.4796	1.5723	1.5401
<i>d</i>	15.357	15.723	13.844	16.245	12.111
<i>f</i>	0.6598	0.9575	1.0605	1.0263	0.6552
$\sqrt{r}$	0.182	0.354	0.458	0.356	0.206
%	84.6	73.9	68.6	73.8	83.3
K	0.0185	0.0357	0.0507	0.0341	0.0233

Mean K, 0.0325. Mean, 76.8%.

## SERIES III.—4 DAYS AT 200°.



<i>b</i>	1.2442	1.1589	1.0294	1.2162	0.7397
<i>d</i>	2.7746	2.9681	2.1431	3.5562	1.9852
<i>f</i>	1.1421	1.0291	0.9068	1.0923	0.6661
$\sqrt{r}$	17.13	13.17	11.04	15.63	15.33
%	5.52	7.06	(8.32)	6.02	6.12
K	0.0079	0.0102	0.0152	0.0077	0.0125

Mean K, 0.0107. Mean, 6.18%.



<i>b</i>	1.6618	1.2455	1.6602	1.4220	0.5721	0.6265	0.7140	0.8029	0.9552
<i>d</i>	2.1555	2.6588	2.7925	2.5879	2.8036	3.1502	2.7022	4.0132	3.8060
<i>f</i>	1.4281	1.0326	1.4200	1.2064	0.4480	0.4928	0.5883	0.3992	0.7593
$\sqrt{r}$	7.10	7.46	7.93	7.85	8.83	9.54	9.80	3.06	8.45
%	12.35	11.83	11.20	11.30	10.18	9.53	9.25	(24.63)	10.58
K	0.0196	0.0194	0.0146	0.0166	0.0223	0.0167	0.0183	(0.0504)	0.0155

Mean K, 0.0175. Mean, 11.67%.

Mean K, 0.0182. Mean, 9.88%.



<i>b</i>	1.3612	1.7145	1.5451	1.4917	1.6890	1.3074	1.6140	1.5117	1.5423	1.4168
<i>d</i>	3.0667	5.2777	4.7000	4.9890	5.8389	5.6442	6.2833	4.3445	4.5112	3.2834
<i>f</i>	0.9430	1.0507	0.6943	0.7521	1.1267	1.2380	1.5159	1.3982	1.4272	1.3104
$\sqrt{r}$	1.00	0.627	0.376	0.425	0.690	2.24	2.22	2.45	2.40	2.86
%	50.0	61.4	72.6	70.2	59.2	30.86	31.06	28.98	29.41	25.90
K	0.1180	0.0507	0.0345	0.0383	0.0535	0.1551	0.1348	0.1940	0.1866	0.2779
Mean K, 0.0590. Mean, 62.7%.						Mean K, 0.1897. Mean, 29.24%.				



## SERIES IV.—8 DAYS AT 200°.



<i>b</i>	1.0176	1.2029	1.0537	0.9397	0.9191
<i>a</i>	1.1893	1.4180	2.0722	1.8208	1.2246
<i>f</i>	0.9168	1.0543	0.8887	0.8018	0.8127
$\sqrt{r}$	9.445	7.785	7.891	8.424	8.959
%	9.57	11.38	11.25	10.61	10.04

Mean, 10.57%.



<i>b</i>	1.1243	1.3382	1.1676	1.0492	1.2360	0.5647	0.5471	0.5713	0.5875	0.5971
<i>d</i>	0.7525	1.4760	1.2375	1.6388	1.9062	1.3600	1.5839	1.9915	2.0335	0.9877
<i>f</i>	1.0235	1.1655	1.0199	1.8932	1.0524	0.4606	0.4335	0.4344	0.4543	0.5059
$\sqrt{r}$	8.102	7.220	7.138	7.307	7.334	7.307	7.028	6.560	6.976	7.384
% (10.98)	12.17	12.29	12.04	12.00	12.04	12.45	(13.24)	12.53	11.93	

Mean, 12.12%.

Mean, 12.24%.



<i>b</i>	1.3746	1.5518	1.3523	1.2130	1.2757	1.2119	1.2702	1.2930	1.3956
<i>d</i>	3.9278	2.5445	3.2222	2.7111	4.8833	2.3777	3.3277	2.6777	3.0222
<i>f</i>	1.0715	1.0606	1.1385	0.9104	1.1982	1.1095	1.1837	1.1873	1.2977
$\sqrt{r}$	1.151	1.242	1.666	1.233	2.242	3.080	2.751	2.991	3.158
%	46.49	44.60	37.51	44.78	(30.85)	24.52	26.67	25.06	24.05

Mean, 43.34%.

Mean, 25.07%.

## SERIES V.—16 DAYS AT 200°.



<i>b</i>	0.7184	0.7728	0.6897	0.5728	0.8302	1.0022
<i>d</i>	0.7300	0.7525	0.6832	0.6445	0.8669	0.8782
<i>f</i>	0.6176	0.6645	0.5860	0.4932	0.7159	0.8709
$\sqrt{r}$	6.186	6.041	5.620	5.916	6.424	6.143
%	13.92	14.20	(15.11)	14.46	13.47	14.00

Mean, 14.01%.



<i>b</i>	1.0044	0.7772	0.7309	0.7169	0.7103	0.8287
<i>d</i>	0.6752	0.5044	0.6494	0.6993	0.7686	0.8057
<i>f</i>	0.8926	0.6987	0.6401	0.6212	0.6113	0.7213
$\sqrt{r}$	6.343	6.950	6.587	6.398	6.588	6.608
%	13.62	(12.58)	13.18	13.52	13.18	13.14

Mean, 13.33%.



$b$	0.6022	0.3434	0.3794	0.5235	0.5324	0.5662
$d$	0.5898	0.7992	0.7428	0.6188	0.2868	0.3158
$f$	0.5157	0.2750	0.3092	0.4481	0.4806	0.5049
$\sqrt{r}$	5.890	6.341	6.496	6.544	6.487	6.561
%	(14.51)	13.62	13.34	13.26	13.36	13.23

Mean, 13.36%.



$b$	1.4745	1.2757	1.4268	1.6301	1.3563	1.4075
$d$	2.3000	1.8944	2.3945	1.7722	2.2778	1.9722
$f$	1.2532	1.0683	1.2117	1.3153	1.1657	1.1783
$\sqrt{r}$	2.838	2.581	2.402	3.468	2.532	2.773
%	26.05	27.92	29.40	22.38	28.31	26.50

Mean, 26.41%.



$b$	1.3518	1.4751	1.5912	1.4601	1.5817
$d$	2.0222	3.6890	4.1222	4.0666	2.9278
$f$	1.2261	1.3785	1.4857	1.3703	1.4623
$\sqrt{r}$	4.352	2.918	2.820	2.785	3.496
%	18.68	25.52	26.18	26.42	22.24

Mean, 23.81%.

## SUMMARY OF RESULTS.

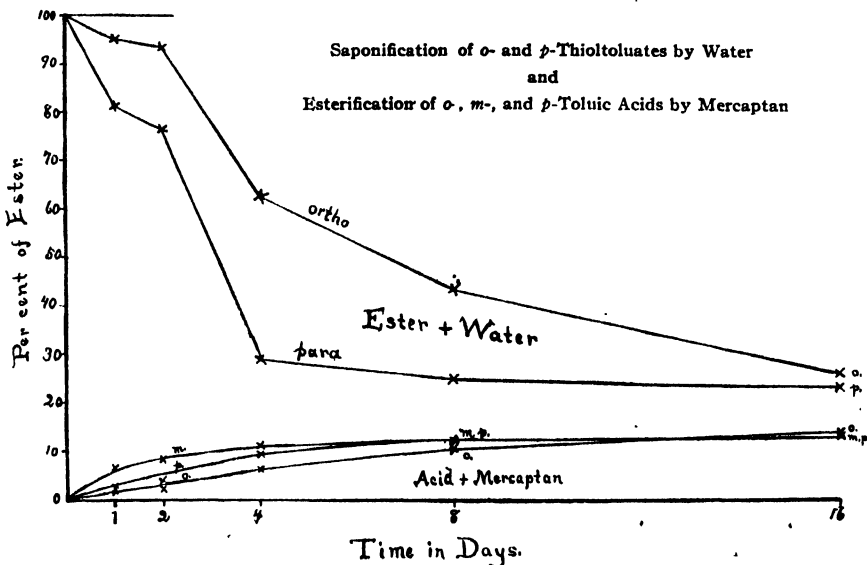
Time.	Acid series.						Ester series.					
	o.		m.		p.		o.		p.			
	%.	K.	%.	K.	%.	K.	%.	K.	%.	K.	%.	K.
1 day.....	1.94	0.0186	6.98	0.0516	3.03	0.0353	95.17	0.0132	81.21	0.063		
2 days....	2.65	0.0069	8.81	0.0298	4.27	0.0174	93.7	0.0077	76.8	0.0325		
4 days....	6.18	0.0107	11.67	0.0175	9.88	0.0182	62.7	0.0590	29.24	0.1897		
8 days....	10.57	.....	12.12	.....	12.24	.....	43.34	.....	25.07	.....		
16 days....	14.01	.....	13.33	.....	13.36	.....	26.42	.....	23.81	.....		

## Discussion of Results.

On examination of the foregoing results, it is seen that very concordant results are obtained in the acid series, while those from the ester series show large variations. Then, too, the same limit is not reached in the ester series that is reached in the acid series. The cause of these discrepancies lies, no doubt, in the fact that in the acid-mercaptan series the reaction mixture forms a homogeneous liquid at  $200^\circ$ ; in the ester-water series, at that temperature, the oily ester and the water remain separated in two layers, thus leaving a comparative small surface of contact at which the reaction takes place.

On the whole, the results for the one and two days' series are rather unsatisfactory, looking at the curves plotted for the progress of the reaction, one sees at once that the reaction seems to lag at two days. As this lag is observed in all five cases it seems probable that the temperature, at which the two days' series was run, was low, due, doubtless, to faulty

regulation of the furnace. A few degrees, at the temperature at which these experiments were carried out, would make quite a large difference in the short periods of time.



The results for the four, eight and sixteen days' series are very good in the acid series. Another series was run for the eight-day period using larger tubes and smaller amounts of water; furnace trouble developed here and the results proved so unsatisfactory that they are not included. In the ester series there seems to be some relation between the amount of water used and the amount of ester remaining. As a rule, the smaller the amount of water used the more ester, relatively, was decomposed. This is opposite to what one would naturally expect.

A study of the results of the rates and limits of the esterification of the three acids is very interesting; one is struck at once by the very large velocity in the case of the meta acid and the small velocity in the case of the ortho acid. The meta acid proceeds over half way to its limit in the first day while the para goes to about one-fourth and the ortho, to about one-seventh their respective limits in the same time. Thus these results agree very well with those obtained by the workers cited in the first part of this paper. It seems that the limits in all their cases are about the same (14%), for there is a very small increase in the results of the sixteen days' series over those gotten at eight days. In the acid-mercaptan series, especially for the longer times, the relative amounts of acid and mercaptan used have no appreciable influence on the limit of the reaction.

In all the experiments run over two days there was a slight amount of

decomposition. This was shown by the presence of hydrogen sulfide which was detected by the lead acetate paper test.

### Conclusion.

- I. Mercaptans esterify acids just as do alcohols.
- II. Mercaptans show the same relations between velocities and limits of esterification of the toluic acids as do alcohols.
- III. The limits in the case of ethyl mercaptan are much lower than in the case of ethyl alcohol.
- IV. The limit in the acid-mercaptan series is independent of the proportions of the reacting substances.
- V. *o*-, *m*- and *p*-Toluic acids reach nearly the same limits of esterification when esterified with ethyl mercaptan.

BALTIMORE, MD.

[CONTRIBUTION FROM CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY.]

## STUDIES IN ESTERIFICATION. VIII.

### THE ESTERIFICATION OF BENZOIC ACID BY ISOMERIC BUTYL MERCAPTANS.

BY J. W. KIMBALL AND E. EMMET REID.

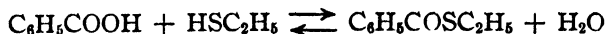
Received September 27, 1916.

### Historical.

The influence of isomerism on the rates and limits of esterification of alcohols has been carefully studied by Menshutkin,<sup>1</sup> who found that the limits for primary alcohols, whether normal or iso-, are practically the same, while those for secondary alcohols are much lower. The limits for tertiary alcohols, he found to be still lower, but the results in this case are not the real limits since a part of the alcohol reacted in another way, decomposing into the unsaturated hydrocarbon and water.

With acetic acid Menshutkin found the following limits for the isomeric butyl alcohols: Normal 67.30%, iso- 67.38%, secondary 59.28%, tertiary 7.10%. The limits are reached in 120 hours at 154°.

Reid,<sup>2</sup> studying the mechanism of the reaction of esterification, employed mercaptans instead of alcohols and showed that the reaction



reaches a well-defined limit as in the case of the oxygen alcohols.

Pratt and Reid<sup>3</sup> then took up this work, using benzoic acid with methyl, ethyl and propyl mercaptans, and accurately determined the limits of these systems. These limits with mercaptans were found to be much lower

<sup>1</sup> *Ber.*, 11, 1507, 2117, 2148 (1878); Liebig's *Ann.*, 195, 334 (1879); 197, 193 (1879); *Ann. chim. phys.*, [5] 20, 289 (1880).

<sup>2</sup> *Am. Chem. J.*, 43, 489 (1910).

<sup>3</sup> *THIS JOURNAL*, 37, 1934 (1915).

than those found by Berthelot and St. Gilles<sup>1</sup> and by Menschutkin<sup>2</sup> with alcohols, but the relations between the limits in the two series are much the same.

As pointed out by Pratt and Reid, it is much more difficult to get concordant results with mercaptans than with alcohols, since the mercaptans must be eliminated before titration of the unesterified acid. The use, in individual experiments, of varying amounts of mercaptan and acid, instead of the identical and equivalent amounts of alcohol and acid such as have commonly been used, also increases the difficulty.

#### Materials.

**Benzoic Acid.**—The benzoic acid used was a well-known firm's best grade.

**Mercaptans.**—The normal mercaptan<sup>3</sup> was prepared from normal butyl bromide and potassium hydrosulfide. The mercaptan obtained was dried over calcium chloride, fractionated several times and the fraction boiling 97–98° used in the work.

The isobutyl mercaptan used was a standard commercial product.

The secondary butyl mercaptan<sup>4</sup> was prepared from secondary butyl bromide and potassium hydrosulfide. The mercaptan was dried over calcium chloride, fractionated several times, and the fraction boiling 83–84° used.

An effort was made to prepare the tertiary mercaptan according to the method of Dobbin,<sup>5</sup> except that tertiary butyl bromide was used instead of the iodide, but only traces of the desired mercaptan were obtained. On account of the difficulties involved, this preparation was abandoned.

**Normal, Iso-, Secondary and Tertiary Butyl Thiolbenzoates.**—The thiol esters were made by alkylating thiolbenzoic acid, prepared according to Kym's<sup>6</sup> directions. The acid was, however, purified by dissolving the potassium salt in water, filtering and liberating the acid with hydrochloric acid. After settling, the oily acid was separated and the aqueous solution extracted with ether. On evaporation of the ether the acid was ready for use. The potassium salt of the purified thiolbenzoic acid was treated, according to the general directions of Wheeler,<sup>7</sup> for the ethyl ester, with the butyl bromide of which the ester was desired. The esters so obtained were carefully fractionated in a partial vacuum. The boiling points and densities of these butyl thiolbenzoates are given in the following table:

<sup>1</sup> *Ann. chim. phys.*, [3] 65, 385 (1862); 66, 5 (1862); 68, 225 (1863).

<sup>2</sup> *Ber.*, 10, 1728 (1877); 11, 1507 (1878).

<sup>3</sup> Grabowsky and Saytzeff, *Liebig's Ann.*, 171, 251 (1874).

<sup>4</sup> Reyman, *Ber.*, 7, 1287 (1874).

<sup>5</sup> *J. Chem. Soc.*, 57, 640 (1890).

<sup>6</sup> *Ber.*, 32, 3533 (1899).

<sup>7</sup> *Am. Chem. J.*, 24, 69 (1900).

Normal.....	160° at 23 mm.	1.0514 25/25
Iso.....	150° at 20 mm.	1.0457 25/25
Secondary.....	151° at 23 mm.	1.0488 25/25
Tertiary.....	110° at 28 mm.	1.0468 25/25

The normal and iso- esters were reddish in color when first prepared but, on standing for several months, the color faded to a light pink. The secondary ester faded from yellow to nearly colorless while the tertiary faded from a very light yellow to colorless. It seems probable that the color is due to some slight impurity.

**Water.**—Conductivity water was used.

#### Apparatus and Procedure.

The same furnace and the same standard solutions were used as in the work of Sachs and Reid in the preceding article. The preparation, filling, heating, and opening of the tubes and the analysis of the reaction products were also the same, except that a longer time was allowed for blowing off the mercaptan remaining. Preliminary experiments with known amounts of benzoic acid and mercaptan showed that it is necessary to pass air through the solutions 25 minutes to remove normal butyl mercaptan, 20 minutes for the iso-, and 15 minutes for the secondary.

The temperature of the heating was 200°.

#### Experimental.

In the first experiments, those given in Tables A to E, the tubes used had an internal diameter of about 4.5 mm. and the rates of esterification in them seem to have been quite different from those in the smaller tubes (3.5 mm. inside diameter) used later, as will be seen from the tables that follow, though Berthelot and St. Gilles<sup>1</sup> state that it is permissible to vary the volume of the unfilled portion considerably without modifying sensibly either the rate or the limit of the reaction.

In their work alcohols and acetic acid were used which do not differ greatly in volatility, but in the present work there is much difference in volatility between benzoic acid and the butyl mercaptans.

In the earlier experiments it was found in the ester-water series that an excess of ester over water gave place to some decomposition which yielded acid, since the results gave too low values for the limit. Samples of esters heated alone in the ordinary tubes to 200° for several days gave considerable acid, showing that the ester-water results could not be relied upon, at least in the case of an excess of ester over water.

Later experiments using an excess of water were run in the smaller tubes and here results were not satisfactory, since equilibrium was not reached in the time allowed, due to the nonmiscibility of ester and water and to the small surface of contact.

— Tubes containing acid and mercaptan and others containing ester and

<sup>1</sup> *Ann. chim. phys.*, [3] 66, 50 (1862).

water in about the usual amounts were heated to  $200^{\circ}$  in a sulfuric acid bath so that the conditions obtaining in the tubes at that temperature could be observed. It was found that, while the acid and mercaptan formed a perfectly homogeneous solution at that temperature, the ester and water still remained in two distinct layers and showed no tendency to mix, separating rapidly after being shaken together. This undoubtedly shows why the esterification proceeds regularly and comparatively rapidly from the acid-mercaptan end, while the mixtures of esters and water are slow to react and yield irregular results.

The results are tabulated according to the plan adopted by Pratt and Reid and used by Sachs and Reid in the preceding article, to which reference must be made for the meaning of the terms and the methods of calculation. To save space, the weights are omitted and the substances are given only in millimols,  $b$  and  $d$  being the amounts put in and  $f$ ,  $g$ , and  $m$  or  $f$ ,  $h$ , and  $k$ , the amounts present at the end. The percentage of esterification, calculated for equivalent quantities, is given in the line marked %.

Some results which are out of harmony with others of the same series are bracketed and are not used in making the averages. All completed experiments, except a few preliminary ones and three from ester-water end, which were cut out to make the tables fit better, are given.

TABLE A.—24 HOURS AT  $200^{\circ}$ .

$C_6H_5COOH + n-C_4H_9SH.$	$C_6H_5COOH + iso-C_4H_9SH.$	$C_6H_5COOH + sec.-C_4H_9SH.$
<i>b</i> 1.6837 1.8623 1.9262 1.9549 2.4359 1.8443 1.8074 1.7009 1.9836		
<i>d</i> 1.1061 1.0783 0.8043 0.8798 1.4866 0.8997 0.9885 1.1150 0.8198		
<i>f</i> 1.5210 1.6761 1.7560 1.8185 2.2775 1.7242 1.6961 1.5773 1.8739		
<i>g</i> 0.9434 0.8921 0.6341 0.7434 1.3282 0.7796 0.8772 0.9914 0.7101		
<i>m</i> 0.1627 0.1862 0.1702 0.1364 0.1584 0.1201 0.1113 0.1236 0.1097		
$\sqrt{r}$ 7.3624 6.5672 7.8050 8.5305 10.980 9.6536 10.949 10.109 10.515		
% 11.96 (13.31) 11.36 10.49 8.55 9.39 8.37 9.00 8.68		
Average, 11.66%	Average, 9.48%	Average, 8.68%

TABLE B.—48 HOURS AT  $200^{\circ}$ .

$C_6H_5COOH + n-C_4H_9SH.$			$C_6H_5COOH + iso-C_4H_9SH.$			$C_6H_5COOH + sec.-C_4H_9SH.$					
<i>b</i>	1.0160	1.2356	1.3576	1.5494	1.1651	0.8882	1.2413	1.0242	1.0373	0.9855	
<i>d</i>	1.4034	1.5321	1.8305	1.2902	0.8687	1.3113	1.1271	1.5676	1.2514	0.9485	
<i>f</i>	0.8562	1.0521	1.1528	1.3605	1.0494	0.7546	1.1310	0.9143	0.9387	0.8127	
<i>g</i>	1.2436	1.3486	1.6257	1.1013	0.7630	1.1777	1.0168	1.4577	1.1528	0.8657	
<i>m</i>	0.1598	0.1835	0.2048	0.1889	0.1157	0.1336	0.1103	0.1099	0.0986	0.0828	
$\sqrt{r}$	6.4573	6.4956	6.6844	6.4799	7.6826	7.0553	9.7322	10.666	10.550	10.130	
%	13.41	13.34	13.02	13.37	11.52	12.42	9.32	8.57	8.66	8.98	
Average,			13.26%	Average,			12.44%	Average,			8.88%



TABLE C.—4 DAYS AT 200°.

$C_6H_5COOH + n-C_4H_9SH.$			$C_6H_5COOH + iso-C_4H_9SH.$			$C_6H_5COOH + sec.-C_4H_9SH.$				
<i>b</i>	1.4601	1.0381	1.2093	1.2609	1.0971	0.9914	1.0496	0.9488	1.2437	0.8611
<i>d</i>	1.6608	1.3812	0.8398	1.5055	1.3950	1.7118	1.2104	1.6153	1.0351	1.4700
<i>f</i>	1.2707	0.8834	1.0811	1.0839	0.9605	0.8399	0.9542	0.8526	1.1555	0.7691
<i>g</i>	1.4714	1.2265	0.7116	1.3285	1.2224	1.5603	1.1150	1.5191	0.9469	1.3780
<i>m</i>	0.1894	0.1547	0.1282	0.1770	0.1366	0.1515	0.0954	0.0962	0.0882	0.0920
$\sqrt{r}$	7.2240	6.7440	6.8479	6.7793	7.9325	7.5562	10.811	11.830	11.860	11.203
%	12.19	12.91	12.76	12.85	11.20	11.69	8.47	(7.79)	(7.78)	8.20
Average, 12.62%			Average, 11.91%			Average, 8.33%				

TABLE D.—8 DAYS AT 200°.

	$C_6H_5COOH + n-C_4H_9SH.$					$n-C_4H_9COSC_4H_9 + H_2O.$				
<i>b</i>	1.7960	1.9123	2.0197	2.1114	1.8779	1.5692	1.5712	1.8220	1.3297	1.7535
<i>d</i>	1.9880	1.5498	1.2603	1.6785	1.2625	2.2480	1.7651	1.6763	0.8992	1.1878
<i>f</i>	1.5709	1.6952	1.8140	1.8784	1.6770	1.4848	1.4249	1.5238	0.8979	1.1764
<i>g</i>	1.7629	1.3327	1.0546	1.4455	1.0616	0.0844	0.1463	0.2982	0.4318	0.5771
<i>m</i>	0.2251	0.2172	0.2057	0.2330	0.2009	0.7632	0.3402	0.1525	0.0013	0.0114
$\sqrt{r}$	7.3930	6.9234	6.7242	7.0722	6.6420	5.8534	6.3860	7.1431	.....	14.504
% (11.91)	12.62	12.95	12.39	13.09	14.59	13.54	(12.28)	.....	(8.12)	
	Average, 12.76%					Average, 14.06%				

	$C_6H_5COOH + iso-C_4H_9SH.$					$iso-C_4H_9COSC_4H_9 + H_2O.$				
<i>b</i>	2.3867	2.0590	2.4883	2.3515	2.0180	1.5548	1.4919	1.6124	1.7711	1.6887
<i>d</i>	1.5177	1.5365	1.5698	1.4189	1.6807	0.9769	1.2878	0.9214	0.9936	0.7882
<i>f</i>	2.1478	1.8321	2.2185	2.1106	1.7732	1.0594	1.1972	0.9288	1.0113	0.8018
<i>g</i>	1.2788	1.3096	1.3000	1.1780	1.4359	0.4954	0.2947	0.6836	0.7598	0.8869
<i>m</i>	0.2389	0.2269	0.2698	0.2409	0.2448	.....	0.0906	.....	.....	.....
$\sqrt{r}$	6.9368	6.8268	6.2971	6.5454	6.5183	.....	7.3326	.....	.....	.....
%	12.60	12.78	13.73	13.25	13.30	.....	(12.00)	.....	.....	.....

Average, 13.15%

	$C_6H_5COOH + sec-C_4H_9SH.$					$sec-C_4H_9COSC_4H_9 + H_2O.$				
<i>b</i>	1.9484	2.0549	2.2958	2.1417	2.0754	1.4806	2.0517	1.6923	1.4631	1.7123
<i>d</i>	1.6475	1.4089	1.6075	1.7562	1.3945	1.3100	2.7032	1.4376	1.2876	1.9705
<i>f</i>	1.8095	1.9147	2.1287	1.9709	1.9365	1.2136	1.9455	1.3723	1.2208	1.5873
<i>g</i>	1.5086	1.2687	1.4404	1.5854	1.2556	0.2670	0.1062	0.3200	0.2423	0.1250
<i>m</i>	0.1389	0.1402	0.1671	0.1708	0.1389	0.0964	0.7577	0.0653	0.0670	0.3832
$\sqrt{r}$	11.90	11.12	10.479	10.343	11.226	7.5645	6.8585	9.4950	9.5818	7.2524
%	7.76	8.25	8.71	8.82	8.18	(11.67)	12.72	(9.75)	(9.45)	12.12

Average, 8.34%

Average, 12.42%

tert.-C <sub>4</sub> H <sub>9</sub> COSC <sub>4</sub> H <sub>9</sub> + H <sub>2</sub> O.					
<i>b</i>	1.6320	1.3179	1.3951	1.2113	1.3014
<i>d</i>	1.3599	2.2425	2.0871	1.6375	1.5375
<i>f</i>	0.7238	0.8118	0.8372	0.7755	0.6857
<i>h</i>	0.9082	0.5061	0.5579	0.4358	0.6157
<i>k</i>	0.6361	1.4307	1.24	0.8620	0.8518
$\sqrt{r}$	0.9501	0.9542	1.0025	1.2653	0.9499
%	51.28	51.17	49.94	44.14	51.28

Average, 49.56%

TABLE E.—12 DAYS AT 200°.

 $C_6H_5COOH + n-C_4H_9SH.$ 

<i>b</i>	1.9435	1.9820	1.8886	2.1827	2.4236
<i>d</i>	1.4300	1.5864	1.8494	1.6663	1.0528
<i>f</i>	1.7175	1.7508	1.6481	1.9374	2.1933
<i>g</i>	1.2040	1.3552	1.6089	1.4210	0.8225
<i>m</i>	0.2260	0.2312	0.2405	0.2453	0.2303
$\sqrt{r}$	6.3658	6.6624	6.7705	6.7640	5.8321
%	13.58	13.05	12.87	12.88	14.64

Average, 13.40%

 $n-C_4H_9COSC_4H_9 + H_2O.$ 

<i>b</i>	1.7139	1.6686	1.5455	1.8926	1.6181	1.8308
<i>d</i>	1.4099	1.2267	1.2822	1.9872	1.7207	2.1537
<i>f</i>	1.3345	1.1913	1.2030	1.6625	1.4264	1.6616
<i>h</i>	0.3794	0.4773	0.3425	0.2301	0.1917	0.1692
<i>k</i>	0.0754	0.0354	0.0792	0.3247	0.2943	0.4921
$\sqrt{r}$	7.8913	9.1513	7.2983	6.0823	6.0055	5.7585
%	(11.25)	(9.76)	(12.33)	14.12	14.27	14.79

Average, 14.39%

 $C_6H_5COOH + iso-C_4H_9SH.$  $iso-C_4H_9COSC_4H_9 + H_2O.$ 

<i>b</i>	2.3318	1.9484	2.1204	2.1991	2.0623	1.7721	2.0594	1.5486	1.5625	1.6675
<i>d</i>	1.7772	1.6519	1.6830	1.6231	1.6619	1.3932	2.0149	2.1592	2.4257	2.1925
<i>f</i>	2.0545	1.6977	1.8527	1.9320	1.8076	1.3264	1.7680	1.4300	1.4625	1.5310
<i>g</i>	1.4999	1.4012	1.4153	1.3560	1.4072	0.4457	0.2914	0.1186	0.1000	0.1365
<i>m</i>	0.2773	0.2507	0.2677	0.2671	0.2547	0.0668	0.2469	0.7292	0.9632	0.6615
$\sqrt{r}$	6.3304	6.1519	6.0464	6.0570	6.2617	7.688	6.5887	4.8646	4.7122	5.0941
%	13.64	13.92	14.19	14.17	13.77	(11.51)	(13.18)	17.05	17.51	16.41

Average, 13.94%

Average, 16.99%

 $C_6H_5COOH + sec-C_4H_9SH.$  $sec-C_4H_9COSC_4H_9 + H_2O.$ 

<i>b</i>	1.5256	2.0172	2.0500	1.3191	1.5289	1.6392	1.4986	1.4718	1.6011	1.8272
<i>d</i>	1.5765	1.3579	2.0202	1.8427	2.0579	1.8928	2.0815	2.0149	1.5320	1.8206
<i>f</i>	1.3931	1.8626	1.8743	1.1850	1.3877	1.5220	1.4165	1.3922	1.4057	1.6337
<i>g</i>	1.4440	1.2033	1.8445	1.7086	1.9167	0.1172	0.0821	0.0796	0.1954	0.1935
<i>m</i>	0.1325	0.1546	0.1757	0.1341	0.1412	0.3708	0.6650	0.6227	0.1263	0.1869
$\sqrt{r}$	10.704	9.6838	10.582	10.603	11.550	7.3009	6.0623	6.2533	8.9480	8.5906
%	8.54	9.36	8.63	8.62	7.97	12.05	14.16	13.78	(10.05)	(10.43)

Average, 8.62%

Average, 13.33%

 $tert-C_4H_9COSC_4H_9 + H_2O.$ 

<i>b</i>	1.4301	1.4445	1.4214	1.3189	1.4348
<i>d</i>	1.8595	1.8262	1.7596	1.4321	1.4709
<i>f</i>	0.8209	0.8317	0.8272	0.7200	0.7371
<i>h</i>	0.6092	0.6128	0.5942	0.5989	0.6977
<i>k</i>	1.0386	0.9945	0.9324	0.7121	0.7338
$\sqrt{r}$	1.0321	1.0654	1.1113	1.1025	1.0302
%	49.21	48.42	47.56	47.56	49.37

Average, 48.38%

TABLE F.—24 HOURS AT 200°.

$C_6H_5COOH + n-C_4H_9SH.$						$C_6H_5COOH + iso-C_4H_9SH.$				
<i>b</i>	1.3806	1.5731	1.5420	1.3601	1.5707	1.7222	1.6403	1.7943	1.9902	1.9402
<i>d</i>	1.3745	1.4810	1.6220	1.4999	1.3967	1.2780	1.2203	1.2092	1.2081	1.2414
<i>f</i>	1.2915	1.4491	1.4049	1.2482	1.4572	1.6220	1.5256	1.6634	1.8543	1.8292
<i>g</i>	1.2854	1.3570	1.4849	1.3880	1.2832	1.1778	1.1056	1.0783	1.0722	1.1303
<i>m</i>	0.0891	0.1240	0.1371	0.1119	0.1135	0.1002	0.1147	0.1309	0.1359	0.1111
$\sqrt{r}$	14.461	11.309	10.535	11.763	12.076	13.794	11.322	10.231	10.375	12.942
%	(6.47)	8.12	8.67	7.84	7.65	(6.76)	8.12	8.90	8.79	(7.17)
Average, 8.08%						Average, 8.60%				

 $C_6H_5COOH + sec.-C_4H_9SH.$ 

<i>b</i>	1.4248	1.8132	1.8492	1.9959
<i>d</i>	1.3424	1.6796	1.6142	1.4810
<i>f</i>	1.3698	1.7129	1.7607	1.9093
<i>g</i>	1.2874	1.5793	1.5257	1.3944
<i>m</i>	0.0550	0.1003	0.0885	0.0866
$\sqrt{r}$	24.145	16.399	18.520	18.841
%	(3.98)	5.75	5.12	5.04
Average, 5.30%				

TABLE G.—48 HOURS AT 200°.

$C_6H_5COOH + n-C_4H_9SH.$						$C_6H_5COOH + iso-C_4H_9SH.$			
<i>b</i>	1.5084	1.5723	1.6370	1.5903	1.7435	1.9525	2.2122	1.8042	1.6895
<i>d</i>	1.6574	1.3912	1.4422	1.3490	1.2259	1.1349	1.1216	1.0218	0.5580
<i>f</i>	1.3644	1.3914	1.4464	1.4130	1.5751	1.7976	2.0092	1.6346	1.5851
<i>g</i>	1.5134	1.2103	1.2516	1.1717	1.0575	0.9800	0.9186	0.8522	0.4536
<i>m</i>	0.1440	0.1809	0.1906	0.1773	0.1684	0.1549	0.2030	0.1696	0.1044
$\sqrt{r}$	9.9790	7.1737	7.0592	7.2571	7.6640	8.5700	6.6923	6.9586	8.1222
%	(9.12)	12.23	12.41	12.11	(11.54)	(10.45)	13.00	12.56	(10.97)
Average, 12.25%						Average, 12.78%			

 $C_6H_5COOH + sec.-C_4H_9SH.$ 

<i>b</i>	1.6354	1.8058	2.1303	1.7739	2.0401
<i>d</i>	1.2459	1.2869	1.6009	1.4866	1.5043
<i>f</i>	1.5535	1.7003	1.9858	1.6499	1.9165
<i>g</i>	1.1640	1.1814	1.4564	1.3626	1.3807
<i>m</i>	0.0819	0.1055	0.1445	0.1240	0.1236
$\sqrt{r}$	16.419	13.434	11.778	12.092	13.149
%	(5.74)	6.93	7.83	7.64	7.07
Average, 7.37%					

TABLE H.—4 DAYS AT 200°.

	$C_6H_5COOH + n-C_4H_9SH.$					$C_6H_5COOH + iso-C_4H_9SH.$				
<i>b</i>	1.5502	1.7820	1.7845	1.9271	1.8451	1.6591	1.7730	1.9730	1.8976	1.9041
<i>d</i>	1.1416	1.2814	1.2081	1.1039	1.3091	1.3690	1.4700	1.4345	1.4189	1.4866
<i>f</i>	1.3779	1.5698	1.5869	1.7220	1.6391	1.4617	1.5535	1.7418	1.6850	1.6814
<i>g</i>	0.9693	1.0692	1.0105	0.8988	1.1031	1.1716	1.2505	1.2033	1.2063	1.2639
<i>m</i>	0.1723	0.2122	0.1976	0.2051	0.2060	0.1974	0.2195	0.2312	0.2126	0.2227
$\sqrt{r}$	6.7070	6.1049	6.4087	6.0655	6.5274	6.6293	6.3466	6.2616	6.7061	6.5427
%	12.98	14.07	13.50	14.15	13.28	13.11	13.61	13.77	12.98	13.26

Average, 13.75%

Average, 13.38%

 $C_6H_5COOH + sec.-C_4H_9SH.$ 

<i>b</i>	1.7444	1.8206	1.7460	2.0770	1.8394
<i>d</i>	1.4777	1.3690	1.3346	1.3967	1.3623
<i>f</i>	1.6166	1.6913	1.6175	1.9327	1.7147
<i>g</i>	1.3499	1.2397	1.2061	1.2524	1.2376
<i>m</i>	0.1278	0.1293	0.1285	0.1443	0.1247
$\sqrt{r}$	11.559	11.208	10.870	10.782	11.692
%	7.96	8.20	8.42	8.49	7.89

Average, 8.19%

TABLE I.—8 DAYS AT 200°.

	$C_6H_5COOH + n-C_4H_9SH.$					$C_6H_5COOH + iso-C_4H_9SH.$				
<i>b</i>	1.6870	1.9836	1.9623	2.0705	1.8025	1.8083	2.1311	1.9222	1.8869	2.1393
<i>d</i>	0.9874	1.2281	1.1072	1.0872	1.0750	1.4688	1.3834	1.3823	1.2913	1.4411
<i>f</i>	1.5094	1.7580	1.7445	1.8534	1.6085	1.5977	1.8976	1.7021	1.6751	1.8994
<i>g</i>	0.8098	1.0025	0.8894	0.8701	0.8810	1.2582	1.1499	1.1622	1.0795	1.2012
<i>m</i>	0.1776	0.2256	0.2178	0.2171	0.1940	0.2106	0.2335	0.2201	0.2118	0.2399
$\sqrt{r}$	6.2252	5.8846	5.7161	5.8496	6.1326	6.7288	6.3233	6.3901	6.3488	6.2963
%	13.84	14.52	14.89	14.60	14.02	(12.94)	13.66	13.53	13.61	13.71

Average, 14.37%

Average, 13.50%

 $C_6H_5COOH + sec.-C_4H_9SH.$ 

<i>b</i>	2.0860	1.8001	1.9197	1.9525	2.0639
<i>d</i>	1.3268	1.4034	1.2348	1.3479	1.5898
<i>f</i>	1.9417	1.6634	1.7832	1.7607	1.9093
<i>g</i>	1.1825	1.2667	1.0983	1.1561	1.4352
<i>m</i>	0.1443	0.1367	0.1365	0.1918	0.1546
$\sqrt{r}$	10.493	10.619	10.252	7.4386	10.707
%	8.70	8.61	8.89	(11.85)	8.54

Average, 8.70%

TABLE J.—12 DAYS AT 200°.

	$C_6H_5COOH + n-C_4H_9SH.$					$n-C_4H_9COSC_6H_5 + H_2O.$				
<i>b</i>	1.6231	1.6075	1.5944	1.2994	1.5117	1.5239	1.6026	1.5594	1.4425	1.4028
<i>d</i>	1.7773	1.7429	1.5532	1.5931	1.5709	3.4525	2.2702	2.9197	2.3535	2.0427
<i>f</i>	1.3827	1.3628	1.3682	1.0920	1.2912	1.0459	1.2704	1.1953	1.1590	1.1047
<i>g</i>	1.5369	1.4982	1.3270	1.3857	1.3504	0.4780	0.3322	0.3641	0.2835	0.2981
<i>m</i>	0.2404	0.2447	0.2262	0.2074	0.2205	2.4066	0.9998	1.7244	1.1945	0.9380
$\sqrt{r}$	6.0630	5.8393	5.9568	5.9342	5.9887	0.9513	2.2045	1.5084	1.9925	2.0892
%	14.16	14.62	14.37	14.42	14.31	51.25	31.21	39.86	33.42	32.37

Average, 14.38%

$C_6H_5COOH + iso-C_4H_9SH.$					$iso-C_4H_9COSC_6H_5 + H_2O.$					
<i>b</i>	2.0311	1.8541	1.3527	1.7288	1.7280	1.4821	1.5496	1.5923	1.6341	1.2957
<i>d</i>	1.7706	1.9559	1.6009	1.6031	1.3490	3.2805	3.6357	2.7143	3.5469	3.1417
<i>f</i>	1.7712	1.5928	1.1482	1.5095	1.5194	1.0069	0.9861	1.2433	1.1464	0.8140
<i>g</i>	1.5107	1.6946	1.3964	1.3838	1.1404	0.4752	0.5635	0.3490	0.4877	0.4817
<i>m</i>	0.2599	0.2613	0.2045	0.2193	0.2086	2.2736	2.6496	1.4710	2.4005	2.3277
$\sqrt{r}$	6.2913	6.2846	6.1919	6.5904	6.3133	0.9687	0.8108	1.7352	1.0596	0.7694
%	13.72	13.73	13.90	13.18	13.67	50.80	55.00	36.56	48.55	56.50

Average, 13.64%

$C_6H_5COOH + sec-C_4H_9SH.$					$sec-C_4H_9COSC_6H_5 + H_2O.$				
<i>b</i>	1.3101	1.4871	1.5616	1.6010	1.7312	1.4811	1.5074	1.3261	
<i>d</i>	1.5776	1.6785	1.6663	1.5665	1.7484	3.1917	4.0409	2.8475	
<i>f</i>	1.1826	1.3492	1.4081	1.4579	1.5837	1.0468	0.9019	0.9272	
<i>g</i>	1.4501	1.5406	1.5128	1.4234	1.6009	0.4343	0.6055	0.3989	
<i>m</i>	0.1275	0.1379	0.1535	0.1431	0.1475	2.1449	3.1390	1.9203	
$\sqrt{r}$	10.271	10.455	9.507	10.066	10.795	1.0850	0.6543	1.0594	
%	8.87	8.73	9.51	9.04	8.48	47.96	60.40	48.50	

Average, 8.92%

$tert-C_4H_9COSC_6H_5 + H_2O.$				
<i>b</i>	1.5115	1.7056	1.6454	1.4657
<i>d</i>	3.8411	3.1195	3.5191	3.6746
<i>f</i>	0.5687	0.6212	0.5976	0.5279
<i>h</i>	0.9428	1.0844	1.0478	0.9378
<i>k</i>	3.2724	2.4983	2.9215	3.1467
$\sqrt{r}$	0.3237	0.3774	0.3416	0.3074
%	75.5	72.6	74.5	76.5

Average, 74.8

TABLE K.—28 DAYS AT 200°.

$tert-C_4H_9COSC_6H_5 + H_2O.$					
<i>b</i>	1.3678	1.4121	1.6289	1.5223	1.3920
<i>d</i>	2.5311	2.7698	2.1259	1.9650	2.2647
<i>f</i>	0.3197	0.3107	0.4458	0.4053	0.3323
<i>h</i>	1.0481	1.1014	1.1831	1.1170	1.0597
<i>k</i>	2.2114	2.4591	1.6801	1.5597	1.9324
$\sqrt{r}$	0.2100	0.1888	0.3162	0.3070	0.2322
%	82.6	84.1	76.0	76.5	81.2

## Summary of Results.

The averages of the results of Tables A and E are brought together in Table L. The figure for the iso- for 4 days is the highest in the run and not the average. The averages from tables F to J are in Table M, while the averages of all experiments with esters and water are grouped in Table N.

TABLE L.—FIRST SERIES.

Esterification of Benzoic Acid by the Butyl Mercaptans.

Time in days.....	1	2	4	8	12
From table.....	A	B	C	D	E
Normal.....	11.66	13.26	12.62	12.76	13.40
Iso.....	9.48	12.44	12.85	13.15	13.94
Secondary.....	8.68	8.88	8.33	8.34	8.62

TABLE M.—SECOND SERIES.

Time in days.....	1	2	4	8	12
From table.....	F	G	H	I	J
Normal.....	8.08	12.25	13.75	14.37	14.38
Iso.....	8.60	12.78	13.38	13.63	13.64
Secondary.....	5.30	7.37	8.19	8.70	8.93

TABLE N.

Ester Remaining when the Butyl Esters of Thiolbenzoic Acid are Heated with Water.

	First Series.		Second Series.	
Time in days.....	8	12	12	28
From table.....	D	E	J	K
Normal.....	14.06	14.39	32.37	..
Iso.....	..	16.99	56.50	..
Secondary.....	12.42	13.33	48.50	..
Tertiary.....	49.56	48.38	74.8	76

The results of Table M are reproduced in the figure.

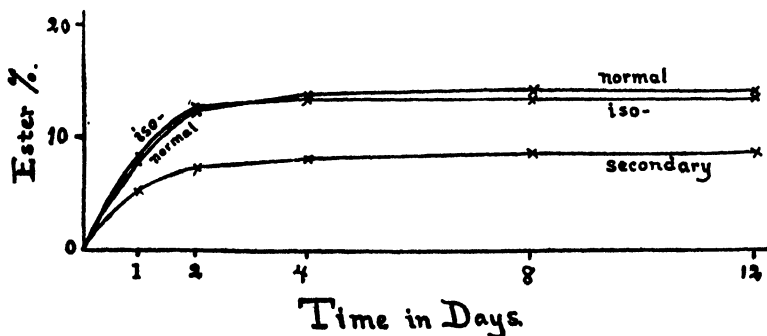


Figure.

Esterification of Benzoic Acid by Normal, Iso- and Secondary Butyl Mercaptans at 200°. Data from Table M.

### Discussion of Results.

A comparison of the data of Tables L and M shows that, in the first series, with the larger tubes, the values for the one- and two day periods are much higher than the corresponding values in the second series, that is, esterification went on much more rapidly in the larger tubes. The limits for the iso- and secondary mercaptans are sensibly the same and are not greatly different for the normal. Whether it was the size of the tubes, giving a larger surface of contact and causing more rapid solution, or whether the difference in velocity of esterification is due to some peculiarity of the surface of the glass, or to some unsuspected cause, it is impossible to say. It is well known that the presence of traces of catalysts and other circumstances have enormous influence on reaction velocities without changing the limits of the reactions. The object of the present study was to find the limits, and the short period experiments were run only to get an idea of the rate of approach to the limits, so as to be sure that the limits had been reached. It is remarkable that the secondary mercaptan, in the first series, reached the limit in one day's time.

The first series is to be regarded as preliminary and much more confidence is felt in the results of the second series, since the accuracy of the work increased with experience. In Tables D and E of the first series the average divergence of individual results, except those bracketed, from the accepted mean is 0.34%, while, in the corresponding Tables I and J in the second series, it is 0.19% or just about half as great.

In Table N, first part, we find that the mixtures of the normal and secondary esters and water reached limits almost exactly agreeing with those obtained from the acid-mercaptan end. There is one result, 13.18, in Table E for the isobutyl ester, which is close to the accepted limit, but most of the values for this ester are higher than this. In the results from the second series, under J, we see that none of the mixtures came anywhere near the accepted limits.

The mixtures of tertiary butyl thiolbenzoate and water do not reach limits such as we would expect. It is more likely that this is a case of decomposition, possibly into butylene and acid, rather than of saponification in the ordinary way. This decomposition seems to have gone considerably further in the large tubes than in the small. Its amount appears to bear no relation to the time of heating, as there was rather less acid found in the tubes that had been heated 28 days than in those not heated so long.

It is seen that both the rates and the limits for the normal and iso-mercaptans are nearly the same, as has been found to be the case with the corresponding alcohols. Both of these are primary mercaptans, and the fact that one is a straight chain and the other a forked chain compound seems to make little difference. The secondary mercaptan, however,

<sup>1</sup> *Compt. rend.*, 132, 38 (1901); 133, 1217 (1901).



In only a very few instances, however, were good yields obtained. Somewhat later Gautier<sup>1</sup> applied this same reaction to cyanhydrines and alkoxy-nitriles, and produced in each case the corresponding ketones.

Grignard<sup>2</sup> allowed a molecule of alkyl or aryl magnesium halide to drop into a molecule of chlorocyan, and was able to obtain fair yields of nitriles, as follows:



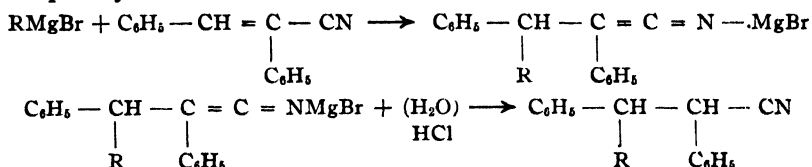
The bromocyan and iodocyan, however, yielded chiefly alkyl or aryl halides



By the same method of procedure with cyanogen, Grignard<sup>3</sup> was able to produce nitriles instead of ketones, which Blaise obtained when he treated the Grignard reagent with cyanogen.

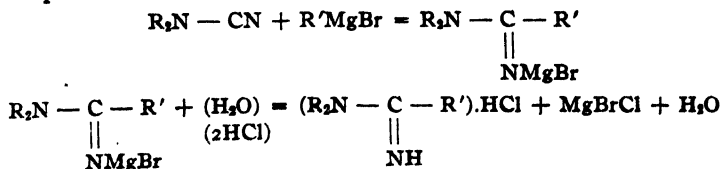


Kohler<sup>4</sup> tried the action of alkyl and aryl magnesium halides on  $\alpha,\beta$ -unsaturated nitriles; 1,4-addition took place, and saturated nitriles were subsequently formed.



Several other types of organic substances exist holding a  $\alpha$ -CN group and these have not been studied; thus cyanamides and their substitution products  $\text{NH}_2\text{CN}$ ,  $\text{NHR}\text{CN}$ , or  $\text{NR}_2\text{CN}$ , acid nitriles  $\text{R} - \underset{\text{O}}{\underset{\parallel}{\text{C}}} - \text{CN}$ ,

and finally the esters of cyanic and thiocyanic acid  $\text{ROCN}$ ,  $\text{RSCN}$ . It seemed to us of scientific interest to know how these substances react with the Grignard reagent, and at the same time it was possible that certain useful synthetic processes might be discovered. As yet we have studied simply the reactions of dibenzyl cyanamide. They ran, as might be predicted, to give first a magnesium halide addition compound, which on decomposition with dilute acid, yielded the salts of substituted amidines.



<sup>1</sup> *Compt. rend.*, 152, 1100, 1259; *Ann. chim. phys.*, [8] 16, 289 (1909).

<sup>2</sup> *Ibid.*, 152, 388 (1910); *Ann. chim.*, [9] 4, 28 (1915).

<sup>3</sup> *Compt. rend.*, 155, 44 (1912).

<sup>4</sup> *Am. Chem. J.*, 35, 386 (1905).

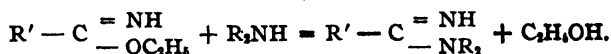
In the laboratory, we treated in ether solution ethyl, phenyl, and tolyl magnesium halides with dibenzyl cyanamide. In each case, when we acidified the reaction mixture, white solids separated between the ether and dilute acid. The substances proved to be the amidine salts, and corresponded in amount to 75% or more of the theoretical yield. Some difficulty was experienced, however, in the purification of these salts for analysis, as they were soluble only in alcohol, water or dilute hydrochloric acid and tended to turn colored during crystallization. In the case of the tolyl we had so much trouble in getting the salt pure enough for analysis that we found it advisable to decompose the salt with sodium hydroxide, extract the free amidine with ether, and treat with phenyl isocyanate, in order to form the urea derivative which crystallized very nicely and was readily purified. The amidines themselves are not easy substances to work with, as most of them are oils or low melting, very soluble solids. Therefore, only in one case, the phenyl dibenzyl amidine, have we isolated and purified the free compound.

Another difficulty which we have just found when using dimethyl cyanamide, and which may be true in other cases, is that the amidine salt is very soluble in water or dilute acid, and so does not separate on acidification of the reaction mixture. This reaction we are studying further, as well as the action of alkyl and aryl magnesium halides on other disubstituted cyanamides, monosubstituted cyanamides, and on cyanamide itself. We expect to study also the action of the Grignard reagent on acid cyanamides, and on the esters of cyanic and thiocyanic acids.

Heretofore substituted amidines and their salts belonging to the type just described, namely,  $R_2N-C-R$ , have been prepared by one method



only, the action of secondary amines on imido-ethers, the other methods available for the amidines in general not being applicable to this particular type of substitution product.



#### Experimental.

**Dibenzylpropionamidine Hydrochloride,  $(C_6H_5CH_2)_2NC(NH)C_2H_5.HCl$ .**  
—Dissolve 2 g. of magnesium in 10 g. of ethyl bromide and dry ether. Cool in ice and allow a dry ether solution of 12 g. of dibenzylcyanamide<sup>1</sup> to flow in drop by drop. The mixture becomes milky in appearance, and solid matter separates. Decompose this directly with hydrochloric acid and ice, thus producing a yellowish solid which floats between the ether and water layers. This, when filtered and dried, weighs 15 g. The ether layer holds a small amount of unchanged dibenzylcyanamide, and

<sup>1</sup> Prepared according to the directions of Diels and Gollmann, *Ber.*, 44, 3164 (1911).

the acid layer nothing but magnesium salts. The solid obtained is soluble in alcohol and acetone, but does not crystallize well from either. From water alone or from water containing a little alcohol, the material forms beautiful rhombohedral crystals, but the yellow color does not disappear, and the m. p. in four recrystallizations does not become constant. Dilute hydrochloric acid and a little alcohol is the best combination, thus it is possible to obtain a constant melting point of  $204-204.5^{\circ}$ . During the crystallization, a very small amount of a second substance, less soluble than the main product and crystallizing in long, fibrous, white needles, is generally obtained, but this was not investigated further.

Calc. for  $C_{17}H_{11}N_2Cl$ : N, 9.69%; Cl, 12.29%. Found: N, 9.65, 9.63; Cl, 12.76, 13.06.

**Dibenzylbenzamidinium Hydrochloride**,  $(C_6H_5CH_2)_2NC(NH)C_6H_5.HCl$ .—Prepare phenyl magnesium bromide from 15 g. of magnesium, 10.2 g. of phenyl bromide and dry ether. Cool with ice and allow 13.9 g. of dibenzylcyanamide in dry ether to drop slowly in. Treat the mixture with ice and hydrochloric acid, and a solid separates between the ether and acid layers. The material on filtering and drying weighs 14 g. Trituration with ether before crystallization served to remove most of the yellowish impurity. The hydrochloride is soluble in acetone, alcohol and chloroform, but on evaporation deposits a glassy mass. The best solvent proved to be a 5% hydrochloric acid containing a little alcohol when large rhombohedra form with a m. p.  $211.5^{\circ}$ .

Calc. for  $C_{21}H_{15}N_2Cl$ : N, 8.35%; Cl, 10.57%. Found: I, N, 8.52, 8.24; Cl, 10.26, 10.38, 10.66.

**Dibenzylbenzamidinium**,  $(C_6H_5CH_2)_2NC(NH)C_6H_5$ .—Grind crystals of dibenzylbenzamidinium hydrochloride to a fine powder, make it into a paste with water, and add strong ammonium hydroxide until excess is present. The solid material changes its appearance under this treatment, and forms pasty-like bunches. Extract with ether. This extract holds all the solid, and after drying it with anhydrous calcium chloride and spontaneous evaporation, a transparent, sticky material deposits which gradually solidifies to hard, white nodules. Yield quantitative. This substance is very soluble in water and all the ordinary organic solvents, and so difficult to purify. From ether it was possible to obtain a constant melting point of  $70-71^{\circ}$ .

Calc. for  $C_{21}H_{15}N_2$ : N, 9.3%; C, 84.0%; H, 6.66%. Found: N, 9.2; C, 83.3, 84.8; H, 5.6, 7.27.

**Dibenzyltoluénylamidinium Hydrochloride**,  $(C_6H_5CH_2)_2NC(NH)C_6H_4CH_3(p).HCl$ .—Treat the Grignard reagent made from 2.1 g. magnesium, 14.5 g. of *p*-bromotoluene and dry ether, after cooling, with 10 g. of dibenzylcyanamide dissolved in ether. Allow the mixture to stand at room temperature a few hours, then decompose with ice and hydrochloric

acid. Filter and dry the solid which separates between the ether and acid layers. A quantitative yield results. This substance proved a very difficult one to purify. Although we tried different combinations of hydrochloric acid, alcohol and water, we were unable to remove the small amount of yellowish impurity, and the analyses for chlorine did not give constant values. We found it advisable, therefore, to make the free amidine and then the phenyl isocyanate derivative.

**Dibenzyltoluénylamidinemonophenyl Ureide**,  $(C_6H_5CH_2)_2NC(NCO-NHC_6H_5)C_6H_4CH_3(p)$ .—Moisten 3 g. of the amidine hydrochloride with water and add a slight excess of concentrated potassium hydroxide solution. Extract with ether, and dry the solution obtained with calcium chloride. On evaporation the free amidine, a yellowish crystalline solid melting at about  $80^\circ$ , and very soluble in all organic solvents, results. Dissolve a known weight of this material in absolute alcohol, and add the theoretical amount of phenyl isocyanate. On evaporation of this solution, fine, white needles in a quantitative yield deposit, which crystallize very readily from alcohol to a constant melting point of  $158^\circ$ .

Calc. for  $C_{29}H_{27}N_3$ : N, 10.0%; C, 80.36%; H, 6.23%. Found: N, 9.75; C, 80.38; H, 6.56.

CAMBRIDGE, MASS.

## ON THE SULFONPHTHALEIN SERIES OF INDICATORS AND THE QUINONE-PHENOLATE THEORY.<sup>1</sup>

By H. A. LUBS AND S. F. ACREE.

Received June 15, 1916.

In developing a method for the colorimetric determination of the hydrogen-ion concentration of bacteriological cultures and culture media, one of us and Clark<sup>2</sup> found that many of the available indicators were unsatisfactory for reasons previously described. On this account a number of new indicators of the methyl red and sulfonphthalein types were synthesized. The phenolsulfonphthaleins had appeared especially promising from the work of White<sup>3</sup> and one of us on this group, not only because the compounds show brilliant color changes but also because their chemical constitution is of such a nature that the substitution of suitable groups should cause their affinity constants to vary to almost any desired degree and give a series of indicators which can be used to measure a wide range of hydrogen-ion concentrations; furthermore, the new compounds ob-

<sup>1</sup> Published by permission of the Secretary of Agriculture as a joint article from the Research Laboratories of the Dairy Division, Bureau of Animal Industry, United States Department of Agriculture, Washington, D. C., and the Forest Products Laboratory, Madison, Wisconsin.

<sup>2</sup> LubS and Clark, *J. Wash. Acad. Sci.*, 5, 609.

<sup>3</sup> *Science*, 42, 101; address at New Orleans Meeting of Am. Chem. Soc., and unpublished dissertation, 1915, Univ. of Wisconsin.

tained would give evidence on the quinone-phenolate theory<sup>1</sup> proposed by one of us. The additional evidence obtained by us from a study of these new compounds and the spectrophotometric data recently by Professor J. S. Guy, confirms so beautifully the theory that there can now be hardly any doubt of its correctness. A further study of the phenolsulfonphthalein series from the standpoint of the quinone-phenolate theory will be continued by Acree and his co-workers by the use of (1) colorimetric, conductivity and catalytic methods, and (2) the hydrogen electrode in order to measure the equilibrium and ionization constants. The "normal and abnormal salt catalysis" by organic and inorganic compounds will be especially investigated by the methods outlined by one of us in earlier papers,<sup>2</sup> in order to try to obtain a series of indicators having only "normal" effects, especially in culture media for fungi. The "salt effects" of organic and inorganic compounds of various classes have been extensively investigated by Clark and Lubs in order to obtain a series of indicators as nearly free from these influences as possible. A preliminary account of this phase of their investigations on the biochemical applicability of indicators will be published shortly.

The phenolsulfonphthalein series was chosen for a further study of the quinone-phenolate theory of indicators because they possess properties which are almost ideal for allowing us to obtain certain crucial data which cannot be secured in the phenolphthalein, rosolic acid, alizarin and analogous series. This theory postulates that the change of color produced in solutions of phenolphthalein by the addition of alkalis is not due chiefly to the rearrangement of a colorless lactoid (A) and the formation of a mono-basic carboxylate salt corresponding to (F), containing a simple colored quinone group, as formerly assumed by others, but arises because of the formation of a quinone group and a phenolate group (G) or its ion. These two groups can combine and form the intensely colored inter- and intra-molecular quinone-phenolate complex (H) similar to the deeply colored double compounds, such as  $O : C_6H_4 : O \cdot 2NaOC_6H_5$ , which Jackson and Oenslager<sup>3</sup> made by combining separate molecules of quinones and alkali phenolates, and which Slagel<sup>4</sup> showed to be formed in aqueous solutions.

Although in the earlier papers the deep colors of the dibasic (carboxylate, phenolate) salts,  $(KOOCC_6H_4)C(:C_6H_4:O)(C_6H_4OK)$ , of phenolphthalein isolated by Meyer and Spengler,<sup>5</sup> and the deep blue color of the potassium and silver phenol salts of the carboxyl esters of phenol-

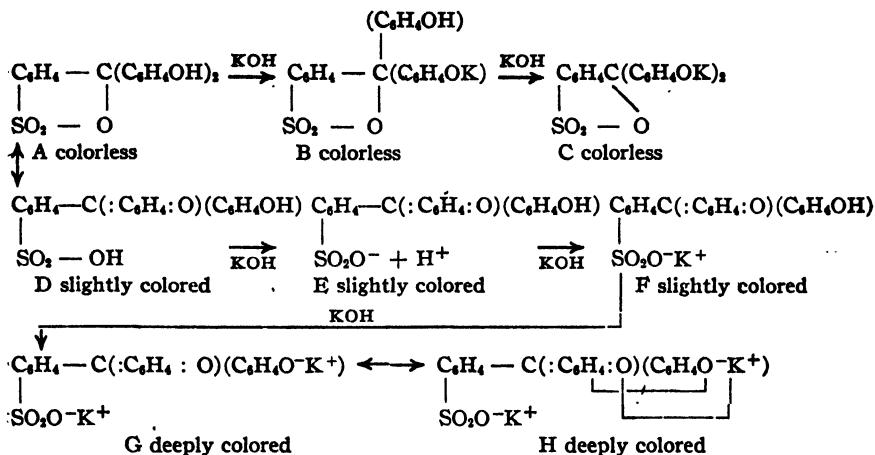
<sup>1</sup> Acree and co-workers, *Am. Chem. J.*, **39**, 528, 789; **42**, 115.

<sup>2</sup> Brunel and Acree, *Ibid.*, **36**, 120; **41**, 474; Slagle and Acree, *Ibid.*, **42**, 130; Loomis and Acree, *Ibid.*, **46**, 586, 632.

<sup>3</sup> *Am. Chem. J.*, **18**, 1; **34**, 441.

<sup>4</sup> *Ibid.*, **39**, 534, 535; **42**, 122.

<sup>5</sup> *Ber.*, **38**, 1318.



phthalein<sup>1</sup> and tetrabromophenolphthalein,<sup>2</sup>  $(\text{ROOCC}_6\text{H}_4)\text{C}(:\text{C}_6\text{H}_4:\text{O})-(\text{C}_6\text{H}_4\text{OK})$ , of aurine,<sup>3</sup>  $(\text{HOC}_6\text{H}_4)\text{C}(:\text{C}_6\text{H}_4:\text{O})(\text{C}_6\text{H}_4\text{OK})$ , and of analogous substances were the basis of the quinone-phenolate theory, we knew that strict logic required the present synthetic work and further quantitative verifications. In other words, the *apparent* color of the dibasic phenolphthalein salts might really arise from admixed deeply colored monobasic salts, just as sodium chloride can be made deeply colored by evaporating it with a solution of a small quantity of dye. Likewise it was clear that the *apparent* color of the phenol salts of the carboxyl esters of phenolphthalein might really arise from the saponification of small amounts of the ester group and the formation of traces of a colored *monobasic* carboxylate salt, whose anion containing a quinone and phenol group would be analogous to the anion of monobasic deeply colored aurine salts containing a quinone and phenol group. This work, therefore, did not disprove absolutely the possibility that the color in all of these cases really arises from small amounts of substances containing a quinone and a phenol group.

The disadvantages encountered in testing this theory in the phenolphthalein series can be readily overcome by using the analogous phenolsulfonphthalein compounds, which differ from the phenolphthaleins simply in that the weak carboxyl group  $-\text{COOH}$ , is replaced by the strong sulfonic acid group  $-\text{SO}_3\text{H}$ , of (D). The phenolsulfophthaleins possess the following advantages:

1. They are much more soluble in water and alcohol and exist to a large extent in the colored quinoidal form of the acid, (D) and (E), whereas the phenolphthaleins are practically only colorless lactoids, (A).

<sup>1</sup> Green and King, *Ber.*, **40**, 3724.

<sup>2</sup> Nietzki, Burckhardt, and Schraeder, *Ibid.*, **28**, 48; **30**, 177.

<sup>3</sup> Friedländer, *Ibid.*, **26**, 172.

2. Whereas the pure slightly colored monobasic salt<sup>1</sup> (F) has not been isolated in the phenolphthalein series, a number of such salts have been made<sup>2</sup> in the phenolsulfophthalein series and their colors and absorption spectra in solution have been shown to be almost identical with those of the free acid (D) and (E) and entirely different in character and intensity from those of the corresponding deeply colored dibasic salts (G) or (H).

3. Their dibasic salts (G) or (H) have been isolated<sup>3</sup> and their colors and absorption spectra in solution are as different in character and intensity from those of the acids (D) and (E) and monobasic salts (F) as are the intense colors of the phenol salts of quinoidal phenolphthalein esters,  $\text{RCOCC}(:\text{C}_6\text{H}_4:\text{O})(\text{C}_6\text{H}_4\text{OK})$  or of aurine,  $(\text{KCC}_6\text{H}_4)\text{C}(:\text{C}_6\text{H}_4:\text{O})(\text{C}_6\text{H}_4\text{OK})$ , from the fainter colors of the corresponding free ester or aurine.

The solubilities of all the phenolsulfophthaleins studied so far are about 100 times those sufficient for a satisfactory study of the color changes. For instance, White<sup>2</sup> has shown that the solubility of phenolsulfophthalein is about 0.03 gram per 100 cc. water, and the other compounds made by him and those since prepared by Lubs<sup>3</sup> and Clark have similar solubilities. The colors of these solutions indicate that considerable quantities of the quinoidal form (D) and (E) are present whose strong sulfonic acid group makes the solution markedly acid. This conclusion has been confirmed by White, who has shown by conductivity measurements that approximately 65% of the phenolsulfophthalein exists in the quinoidal form.

The strongly acid properties of the phenolsulfophthalein series are in marked contrast to those of the weak phenolphthaleins. The carboxyl and phenol groups of phenolphthaleins differ so little in strength and the alkali is partitioned between them to such an extent that visible quantities of the "dibasic quinoidal carboxylate phenolate salt" (G) and (H) are formed by the addition of the smallest quantities of standard alkalies. On the other hand, a consideration of the phenolsulfophthaleins corresponding to (D) and (E) shows that the molecule contains a very weak phenol group which is suppressed still more in ionization by the strong sulfonic acid with an affinity constant close to those of the strong mineral acids. This series was chosen for the present studies because it was predicted that they would act as "self-indicators" and that a large fraction of one molecule of alkali would be neutralized by the strong sulfonic acid group before the useful  $\text{P}_\text{H}$  range would be reached, or, to be more explicit, before any *phenol* salt could be formed and an appreciable

<sup>1</sup> Kober and Marshall, *THIS JOURNAL*, 34, 1431, 1432, isolated the colorless carbinol monobasic salts.

<sup>2</sup> White, Dissertation, New Orleans address, *Science*.

<sup>3</sup> *Loc. cit.*

change of color occur. The experimental evidence has confirmed this prediction and the quinone-phenolate theory. Small quantities of added alkali are first neutralized practically completely by the strong sulfonic group without any appreciable change of color and a simultaneous tautomeric rearrangement of (A) into (D) ensues. As fast as the sulfonic acid is neutralized the ionization of the remaining portion is suppressed more and more by the increasing amount of sulfonate anions formed and finally becomes so small that the alkali is neutralized very appreciably by the hydrogen ions from the phenol groups and the *intense, different* color of the dibasic quinone-phenolate salt and its anion appears. The amount of alkali necessary to produce this sharp change of color is about 0.85–0.87 molecule in the case of phenolsulfophthalein, and about 0.98 molecule in the case of thymolsulfophthalein, and hence will necessarily depend upon both (a) the value of the constant for the equilibrium between the lactoidal and quinoidal structure, and (b) the relative magnitudes of the affinity constants of the sulfonic acid and of the phenol. The equilibrium constants under (a) are being measured and are therefore not adequately treated in this paper. By substituting negative bromo or nitro groups in the  $-\text{C}_6\text{H}_4\text{SO}_3\text{H}$  residue, the affinity constant of the  $-\text{SO}_3\text{H}$  group is increased, while that of the phenol group and the  $P_H$  ranges are not changed.<sup>1</sup> Phenolsulfophthalein and phenol-nitrosulfophthalein<sup>1</sup> have the same  $P_H$  range, 6.8–8.4, and thymolsulfophthalein and thymolnitrosulfophthalein<sup>1</sup> have the same  $P_H$  range, 8.0–9.6. The ionization of the phenol group is simply suppressed more by the nitrosulfonic acid group and nearly one molecule of alkali can be added before the deeply colored dibasic salt is visible. By the substitution of negative bromo or nitro groups in the phenol residue, however, the affinity constant of the phenol groups is greatly increased. For example, the affinity constant of phenol, about  $10^{-10}$ , is increased about 700 times or to  $6.8 \times 10^{-8}$ , by the introduction of one nitro group in the ortho position, and increased about 2,700,000 times, or to  $2.7 \times 10^{-4}$ , by its conversion into *o,o*-dinitrophenol. It follows then that the introduction of these negative groups into the phenol residues of (D) by the ordinary substitution methods should, and does, make the phenol group much stronger and hence a smaller  $P_H$  value will still give enough phenolate anions to begin to give the color; in other words, the addition of smaller amounts of bases will cause the intense color changes in these substituted compounds. On the other hand, the substitution of methyl, isopropyl or amino groups in the phenol residues should, and does, lower the affinity constant of the phenol group and raises the  $P_H$  rays from 6.8–8.4 for phenolsulfophthalein to 7.2–8.8 for *o*-cresolsulfophthalein and 8.0–9.6 for thymolsulfophthalein. These alkyl groups, therefore, raise the 0.85

<sup>1</sup> See Lubs and Clark, *J. Wash. Acad. Sci.*, 6, 483 (1916).



mol alkali required to change the color of the phenolsulfophthalein to about 0.95–0.98 molecule of alkali required to raise the  $P_H$  value enough to give the intense color change in *o*-cresolsulfophthalein and thymolsulfophthalein. The introduction of two bromine atoms into the thymol groups then raises the affinity constant of the thymol phenol group and lowers to 0.90–0.92 molecule the amount of alkali necessary to give the  $P_H$  value required for the intense color change.

In general, the introduction of negative chloro, bromo, nitro, etc., groups into the phenol residues might be expected to change the  $P_H$  range in a fairly regular manner for all these compounds. It is, therefore, interesting to note<sup>1</sup> that the difference between the  $P_H$  ranges for thymolsulfophthalein, 8.0–9.6, and for dibromothymolsulfophthalein, 6.0–7.6, is about 2.0, which is the same as the difference between the useful  $P_H$  range for *o*-cresolsulfophthalein, 7.2–8.8, and dibromo-*o*-cresolsulfophthalein, 5.2–6.8. This value 2.0 is also just half the difference between the  $P_H$  ranges for phenolsulfophthalein, 6.8–8.4, and tetrabromophenolsulfophthalein, 2.8–4.6. We expect to study these relations for a large number of such compounds. It is only fair to state that it is difficult to purify some of these indicators and that some of the quantitative data given in this paper may be modified later.

There is now evidence<sup>2</sup> at hand to show that the source of intense color in these solutions is chiefly the inter- or intra-molecular combination of a quinone and a phenolate ion in (G) and (H) and not simply the quinone and non-ionized phenolate salt. In solutions of the free tetrabromo- and tetranitro-phenolsulfophthalein and of the dinitro-thymolsulfophthalein the phenol groups are highly ionized and give clearly, *without the addition of any alkali*, the colors characteristic of the nearly completely ionized dibasic salts. The addition of strong mineral acids suppresses the ionization of the phenol group and discharges the intense color of the quinone-phenolate ion. The intense color would not fade if it came from the nonionized quinone-phenolate grouping. That the quinone group actually combines with the phenolate ion is shown by the fact that the yellow band characteristic of the spectrum<sup>3</sup> of the free acid and monobasic salt, and hence coming from the quinone group, disappears when the dibasic salt is formed. All phases of this problem will be studied by the use of the phenolsulfophthaleins and their salts, esters, and other derivatives.

**Phenolsulfophthalein.**—White showed that when eleven parts of pure crystalline anhydride of sulfobenzoic acid are fused with 12 parts of phenol at 140° for 6 hours, as described, by Remsen,<sup>4</sup> Sohon, and Holmes,

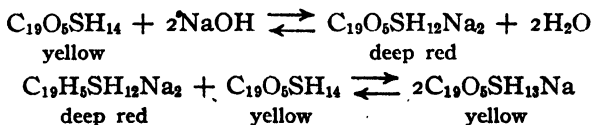
<sup>1</sup> Lubs and Clark, *J. Wash. Acad. Sci.*, 6, 483 (1916).

<sup>2</sup> White, New Orleans address, *Science*, 42, 101.

<sup>3</sup> White, Dissertation, New Orleans address, *Science*.

<sup>4</sup> *Am. Chem. J.*, 20, 257; 25, 201.

the mass becomes pasty. It is allowed to cool and is boiled with water and filtered. The same compound has been made by Lubs<sup>1</sup> and Clark by heating the acid chloride and phenol. The red powder is dissolved in dilute alkali and reprecipitated by addition to hot dilute hydrochloric acid. When washed repeatedly with hot water the powder is practically pure. It can be recrystallized from phenol by the addition of ether. The acid is soluble in water to the extent of about 0.3 g. per liter. It is yellow in slightly acid solution, pink in stronger acids, and purple in weak alkalies. Stronger alkaline solutions discharge the color, probably through hydration, and the colorless solution becomes colored again on the addition of acids. When an excess of the solid is agitated with alkaline solutions, or with carbonates or with oxides of the heavy metals, yellow or orange solutions of the monobasic<sup>2</sup> salts are formed, and these salts can be isolated by evaporation of the solutions *in vacuo*. The addition of two molecules of an alkali to the acid produces the deep red dibasic salt and the addition of soluble salts of heavy metals does not produce deep red precipitates of the dibasic heavy metal salts. Solutions containing about 0.03 g. phenolsulfophthalein in 100 cc. water are yellow or orange in color. The addition of 0.01 *N* alkali produces *locally* the deep red color of the dibasic salt where the drop of alkali falls, but this color disappears immediately when the solution is stirred and the dibasic salt is changed to the yellow monobasic salt as follows:



This set of reactions can be continued until about 0.85–0.87 molecule of alkali is added and the red color becomes faint and permanent. It then requires about 2% more 0.01 *N* alkali to change the color into a decided red, which increases in intensity by the addition of more alkali. This set of color changes is characteristic of all the analogous sulfophthaleins, only the quantitative relations and colors varying in different cases.

The following data<sup>3</sup> show the amount of alkali required to produce the permanent color change. Carbon dioxide must be rigidly excluded in the titration of all these sulfophthaleins. Approximately 0.02 *N* alkali was found to be suitable for the titrations. In the column headed "Cc. NaOH, theory" are given the number of cubic centimeters of alkali calculated for the sulfophthalein as a monobasic acid, and Columns 5 and 6 give the amount and per cent. of one molecule actually required.

<sup>1</sup> *Loc. cit.*

<sup>2</sup> White, Dissertation, etc.

<sup>3</sup> A new standard alkali solution was used in this and succeeding titrations, which accounts for the fact that 8 required a larger volume of alkali than did 6, although Sample 8 was smaller than Sample 6.

No.	Wt. of phthalein.	Vol. of solution. Cc.	Cc. NaOH theory.	Cc. NaOH found.	Per cent. of 1 molecule. Eq.
1	0.0314	300	4.28	3.75	87.6
2	0.0310	150	4.28	3.73	87.1
3	0.0288	125	3.99	3.43	87.2
4	0.0322	200	4.40	3.77	85.6
5	0.0176	200	2.40	2.10	87.5
6	0.0420	150	5.73	4.97	86.6
7	0.0131	100	1.73	1.51	87.2
8	0.0389	300	5.95 <sup>1</sup>	4.76	80.0
9	0.0329	300	5.03	3.96	78.7
10	0.0297	300	4.54	4.11	90.5
11	0.0252	300	3.86	3.49	90.4
12	0.0329	300	5.04	4.41	87.5

Average, 86.3

Titration 1 to 6, inclusive, were made with material obtained from Hynson, Westcott & Company, Baltimore. The others were made with material of our own preparation,<sup>1</sup> 10, 11 and 12 having been crystallized from phenol by the method already described.

The color changes of phenolsulfophthalein are produced in solutions varying in hydrogen-ion concentration from  $P_H$  6.50 to  $P_H$  8.50, and are very sharp between  $P_H$  7 and  $P_H$  7.5. Six drops of a 0.012% yellow solution of the monosodium<sup>2</sup> salt make an excellent indicator when diluted with 50 cc. of water and give a distinct purple color when only 0.01 cc. 0.1 *N* alkali is added.

**Tetrabromophenolsulfophthalein.**—This substance was prepared by White by the action of bromine on phenolsulfophthalein in glacial acetic acid. It melts at  $270-1^\circ$ . A concentrated aqueous solution is orange in color with a tinge of blue. The addition of hydrochloric acid decreases the ionization of the phenol group, discharges the blue color, and makes the solution yellow or orange in color. When this solution is diluted and the phenol group ionizes more the blue color comes out strongly again and the addition of alkali makes the solution intensely blue. The addition of hydrochloric acid again discharges the blue color. For example, 12 drops of 0.04% alcoholic solution of the tetrabromo compound added to 50 cc. water gave a solution whose blue color was distinctly discharged by the addition of 0.5 cc. 0.01 *N* hydrochloric acid. The larger affinity constant of the bromophenol group causes the color changes to take place sharply between  $P_H$  3.2 and  $P_H$  4.5. Three to six drops of a 0.04% alcoholic solution of the acid make an excellent indicator.

**Tetranitrophenolsulfophthalein.**—This compound was made by White

<sup>1</sup> White, Dissertation.

<sup>2</sup> Aqueous solutions of the monosodium salts of all of the sulfophthaleins can be used as indicator solutions.

by treating phenolsulfophthalein with a mixture of concentrated sulfuric and nitric acids. The compound is yellow in strongly acid solutions, but purple in water because of the large ionization of the nitro-phenol group. The addition of alkali does not appreciably increase the depth of the purple color but the addition of strong hydrochloric acid causes this to fade to yellow, which is changed to purple again when the solution is diluted and the ionization of the nitro-phenol group is increased. The large affinity constant of the nitro-phenol group is shown by the fact that White found a molecular conductivity of about 430 for this substance in  $N/1000$  solution, of which value about 370–80 as a maximum comes from the sulfonic acid group. The nitro-phenol group is too strong an acid to allow this substance to be a valuable indicator for most work. An excess of alkali causes the purple color to fade to yellow, which immediately changes to purple again when the excess of alkali is neutralized.

***o*-Cresolsulfophthalein.**—This indicator can be prepared either by the method of Remsen and Sohon or that of Lubs and Clark. The fusion of *o*-cresol with either the anhydride or chloride of sulfobenzoic acid gives about 50% yield. The *o*-cresolsulfophthalein can be recrystallized from glacial acetic acid and is soluble in alcohol and water. It is yellow in very dilute acid solution and purple in dilute alkalies. Two to four drops of a 0.4% alcoholic solution make an excellent indicator. Six drops of a 0.2% alcoholic solution added to 50 cc. water gave a distinct color change when 0.01 cc. 0.1 *N* alkali was added. The color changes are produced in solutions having  $P_H$  7.2 to  $P_H$  8.8.<sup>1</sup> The titration of *o*-cresolsulfophthalein with dilute alkalies shows clearly that the cresol group is so weak that practically one molecule of alkali is neutralized by the sulfonic acid group before sufficient phenolate salt is formed to change the color from orange to purple. For example, 0.0567 gram required 14.5 cc. 0.01 *N* alkali, or 98% of the theory, instead of the calculated 14.83 cc. alkali. The alkaline solution shows color phenomena characteristic of nearly all of these sulfophthaleins. A deep blue color is observed in reflected light. In transmitted light the solution appears deep red and the spectrum shows only a red band.

**Thymolsulfophthalein.**—This substance was prepared by Lubs and Clark by fusing the acid chloride with thymol in the presence of dehydrated zinc chloride 4 hours at 140° with frequent stirring. The melt was boiled with water and the hardened mass was extracted with alcohol to remove the remaining thymol. The cold alcoholic solution gave a precipitate of the thymolsulfophthalein as greenish crystals. The substance is yellow in very dilute acids, pink in concentrated acids, and deep blue in dilute alkalies when viewed by reflected light but deep red in transmitted light. The color changes take place between  $P_H$  8 and  $P_H$  9.75.

<sup>1</sup> Lubs and Clark, *J. Wash. Acad. Sci.*, 6, 483.

and the useful range lies between  $P_H$  8 and  $P_H$  9.5, which is about the same as that of phenolphthalein. Three to six drops of a 0.04% alcoholic solution makes an excellent indicator. For example, 12 drops of a 0.04% alcoholic solution added to 50 cc. water give a distinct green color change when 0.01 cc. 0.1 *N* alkali is added; 0.02 cc. makes the solution blue.

The isopropyl and methyl groups lower considerably the ionization of the phenol group and make it necessary to add practically one molecule of alkali before the blue color of the dibasic salt becomes visible. Titration of samples kindly furnished by Mr. H. A. B. Dunning showed that 0.0548 g. required 11.50 cc. 0.01 *N* alkali, or about 0.98 molecule instead of the theoretical 11.75 cc. Material prepared by Lubs gave the following data: 0.0564 g. required 11.70 cc., or 0.967 molecule, instead of the theoretical 12.10 cc.; 0.0560 g. required 11.60 cc. or 0.967 molecule instead of the theoretical 12.01 cc. As it requires only about 0.02 molecule of alkali to change the color decidedly from that of the orange-free acid and monobasic salt to the deep blue of the dibasic salt, it is clear that the thymolsulfophthalein gives excellent substantiation of the quinone-phenolate theory that the intense color change is not due to a monobasic salt and simply to the quinone group, but arises from the formation of a compound formed by the union of a quinone and a phenolate ion.

**Dibromothymolsulfophthalein.**—This indicator was prepared by Lubs and Clark by the action of bromine in glacial acetic acid on the thymolsulfophthalein and is obtained in yellow crystals. It is yellow in acid solution and deep blue in dilute alkalies when viewed by reflected light but red in transmitted light. The best color changes occur between the ranges of  $P_H$  6 and  $P_H$  7.25. About 2 drops of a 0.04% alcoholic solution make an excellent indicator, and become distinctly green in 50 cc. water when 0.005 cc. 0.1 *N* alkali is added; 0.01 cc. makes the solution blue.

The influence of the negative bromo groups in increasing the ionization of the phenol group is made clearly evident by the fact that less alkali is required to give the blue color than was found to be necessary with thymolsulfophthalein. For example, 0.0628 g. of a sample prepared by Dunning required 9.2 cc. 0.01 *N* alkali, or 0.91 molecule, instead of the theoretical 10.06 cc. Of material prepared by Lubs and Clark 0.0555 g. required 7.55 cc. 0.01 *N* alkali, or about 0.85 molecule, instead of the theoretical 8.89 cc. and 0.0643 g. required 9.50 cc. 0.01 *N* alkali, or about 0.92 molecule, instead of the theoretical 10.30 cc.

**Thymolnitrosulfophthalein.**—This compound was made by Lubs and Clark by heating thymol with the acid chloride of nitrosulfobenzoic acid and dehydrated zinc chloride. The subsequent treatment was like that for thymolsulfophthalein. It forms a powder which appears red or green-

ish blue, depending upon its fineness of subdivision and the way in which it is illuminated. It is yellow in dilute acids and deep blue in dilute alkalis in reflected light and shows a red and a violet band in transmitted light. This compound was made because it was predicted that the nitro group in the benzene sulfonic acid residue would increase the affinity constant of the sulfonic acid group more than that of the phenol group and that practically one molecule of alkali must be added before the intense color of the dibasic salt is observed. The experiments verify the theory. For example, 0.0415 g. requires theoretically 8.12 cc. 0.01 *N* alkali to neutralize the sulfonic acid group. The concentrated aqueous solution of this amount of the indicator is orange in color and the addition of 7.92 cc. or 0.98 molecule produces no change of color; when 8.02 cc., or 0.99 molecule of alkali, are added the blue color of the dibasic salt just began to appear. When 8.22 cc. or about 1.01 molecule of alkali were added there was a distinct change of color. When 0.67 cc. more 0.01 *N* alkali was added the color of the solution was dark green, when 1.2 cc. were added the solution was very dark green, and when 2.15 cc. were added the solution was bluish green. A total of two or more molecules of alkali made the solution dark blue in color. In another experiment 0.0435 g. was dissolved in about 200 cc. of hot water and titrated with 0.01 *N* alkali. One molecule of alkali corresponds to about 8.6 cc. alkali, and it required 8.2 to 8.3 cc., or about 0.96 molecule to produce any noticeable change in color. The addition of 8.5 cc. 0.1 *N* alkali made the solution dark red, 8.7 cc. made the solution very dark, 9.63 cc. made the solution olive-green, and 10.0 cc. made the solution a decided green in color. The addition of an excess of alkali made the solution deep blue and boiling the solution did not cause the color to fade perceptibly through the well-known hydration phenomenon. The excellence of this indicator is shown by the fact that 4 drops of a 0.04% alcoholic solution added to 50 cc. water required only 0.01 cc. 0.1 *N* alkali to give a distinct green color; 0.02 cc. makes the solution blue. The color changes take place between  $P_H$  8.2 and  $P_H$  9.6.

#### Conclusions.

1. Solutions of sulfophthaleins having no negative bromo or nitro groups in the phenol residues are yellow or orange in color; the colors and conductivities show that the indicators exist largely in the quinoidal form. They are "self-indicators" and can be titrated with from 0.85 to 0.98 molecule of alkali before the intense color change due to the dibasic salt is observed. The monobasic sulfonic acid salt (F) has practically the same orange or faint red color as the free, nearly completely ionized acid. All these facts make untenable theories formerly proposed by others that the intense color changes in the phenolphthalein series arise simply from the quinone group. The data give further evidence for the quinone-

phenolate theory that the intense purple or blue color is produced only when appreciable quantities of the dibasic quinone-phenolate salts are formed, which then give rise to the combination of the quinone group and the phenolate anion. The introduction of negative groups into the benzenesulfonic acid residue increases the affinity constant of this group but does not alter appreciably the affinity constant of the phenol group or the  $P_H$  range.

2. Solutions of sulfophthaleins having negative bromo or nitro groups in the phenol residues have high molecular conductivities and low  $P_H$  ranges, which fact indicates considerable ionization of the phenol residue. In harmony with this idea is the fact that these solutions exhibit more or less the colors of the dibasic alkaline salts. In conformity with these conclusions is the fact that the addition of mineral acids to solutions of these sulfophthaleins suppresses the ionization of the phenol group and changes the intense color characteristic of the dibasic salts into the fainter yellow or orange characteristic of the quinone group. In the *solid state* these bromo- and nitrophenol derivatives are yellow, while the sulfophthaleins with no negative groups in the phenol residues, or having negative groups in the benzenesulfonic acid group, are generally dark brick-red.

3. The fact that 0.98 molecule of alkali can be added to *o*-cresolsulfophthalein before the deep color appears shows that practically all of the monobasic salt exists as (F) and almost none as the colorless form (B) and that practically all of the dibasic salt is in the forms (G) and (H) and practically none in the colorless form (C). This monobasic salt is, therefore, nearly an ideal indicator because practically none of the alkali and indicator is wasted in forming colorless hydrated or lactoidal salts (C) but all is consumed in the formation of the deeply colored dibasic salts (G) and (H). These relations may vary for the different members of this group. This point is very important in the proposed equilibrium studies of these compounds and no such evidence can be obtained in the phenolphthalein series.

4. The free sulfophthaleins and the monobasic salts give absorption spectra containing a yellow band characteristic of the quinones. When the dibasic salt is formed this yellow band disappears and a deep red band appears. This indicates that the quinone group as such disappears because it combines with the phenolate anion and forms a complex quinone-phenolate group.

5. Solutions of the dibasic salts of some of these sulfophthaleins have different colors when viewed in reflected and then in transmitted light. This phenomenon has been noted by one of us in solutions of crystal violet and other substances and is being investigated to learn the charac-

teristics of the "reflection and transmission spectra" for each of these substances.

6. Solutions of some sulfophthaleins which are yellow in neutral or faintly acid solutions become red in stronger acids and, hence, have been found by Mr. Homer Cloukey to be colored red by such salts as zinc chloride and stannous chloride. But even some neutral salts, such as sodium chloride, change the colors of these solutions and this "salt effect" of acids, bases and salts will be extensively investigated.

7. On account of all of these characteristics of the sulfophthaleins it has been found possible to prepare a series of indicators having a wide range of sensibility of hydrogen ions. By substituting bromo, nitro, methyl, isopropyl, amino and other groups in the benzenesulfonic acid group, and especially in the phenol residue, one is enabled to change the ionization constants of the sulfonic acid and phenol groups greatly and hence prepare indicators covering a wide range of usefulness. The phenol, thymol, and cresolsulfophthaleins, and their bromo derivatives, are highly satisfactory indicators.

DAIRY DIVISION, BUREAU OF ANIMAL INDUSTRY, WASHINGTON, D. C.  
FOREST PRODUCTS LABORATORY, MADISON, WISCONSIN.

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[CONTRIBUTIONS FROM THE LABORATORIES OF ORGANIC ANALYSIS AND FLORICULTURAL  
CHEMISTRY OF THE UNIVERSITY OF ILLINOIS.]

## EFFECTS OF LARGE APPLICATIONS OF COMMERCIAL FERTILIZERS ON CARNATIONS.\*

BY GEORGE D. BEAL AND FRED WEAVER MUNCIE.

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In the investigation of the use of commercial fertilizers in growing carnations by the Illinois Agricultural Experiment Station, it has been found that the lack of appreciation by florists of the relatively high plant food concentrations and often high solubilities of commercial fertilizers, as compared with manure, has often led to a complete loss of a crop of flowers in an effort to produce an extraordinarily large one. On this account, it was considered desirable to study the causes and effects of overfeeding with the more ordinarily used commercial fertilizers.

The fertilizers chosen for the experiment were dried blood, sodium nitrate and ammonium sulfate, acid phosphate and disodium phosphate, and potassium sulfate. For comparison, sodium chloride and sodium sulfate also were used on some sections. Experimental work upon the subject was carried out during the years 1912-15.

Carnations are propagated by means of cuttings, and from these it was

\* This paper presents the data contained in the thesis presented by Mr. Muncie in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry in the Graduate School of the University of Illinois.



found impossible to secure a normal growth in either sand or water cultures. Hence, the experimental work was based upon the study of plants grown in soil carefully selected with the view to securing uniformity throughout the benches, watered to give as nearly as possible the same moisture content, and subjected very nearly to identical conditions of heat, ventilation, and illumination. For details regarding the type of soil, its preparation, arrangement of sections, etc., the reader is referred to *Bull.* 176 of the Illinois Agricultural Experiment Station.

The method consisted of weekly applications of the fertilizers at various rates upon isolated sections in the benches, beginning about October 1 and continuing until about May 1 or until injury became serious.

**Effects of Overfeeding on Condition of Plants.**—The rapidity with which the sections of carnations became affected followed in a general way the solubility of the fertilizer used.\* The solubilities\*\* of the pure substances in water per hundred parts at 0° are given in Table I.

TABLE I.—SOLUBILITIES OF PURE SALTS IN WATER AT 0°. (PARTS PER 100.)

NaNO <sub>3</sub>	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	NaCl	KCl	K <sub>2</sub> SO <sub>4</sub>
72.9	71.0	35.7	28.5	8.5
Na <sub>2</sub> HPO <sub>4</sub> ·12H <sub>2</sub> O	CaH <sub>4</sub> (PO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O	CaHPO <sub>4</sub>	CaSO <sub>4</sub> ·2H <sub>2</sub> O	
6.3	4 (15°)	0.028	0.241	

Commercial acid phosphate consists of about equal parts of mono-calcium phosphate and calcium sulfate. Reversion to monohydrogen phosphate in presence of bases in the soil would further decrease the low solubility of the acid phosphate and by double decomposition with calcium, iron and other bases in the soil render the sodium phosphate first applied less soluble, as pointed out by Cameron and Bell.<sup>7</sup>

Dried blood, giving soluble products at a rate depending upon the rapidity with which bacterial decomposition proceeds, could not be rated as having a known solubility without a study of the bacteriological activity of the soil mixture. Tests with litmus paper showed that the surface of the soil, neutral at the beginning of the experiment, became acid seven or eight days after the addition of the dried blood. Soil to which ammonium sulfate was applied became acid as quickly also.

Single applications of ammonium sulfate and sodium chloride at the rate of 12.5 kg. per 100 sq. ft. made on December 3, 1913, produced marked injury within a week's time. Equal amounts of potassium sulfate, at this time, followed by further applications at intervals of one or two weeks, at the rate of 1.25 kg. per 100 sq. ft., produced no signs of injury

\* The impurities in the ammonium sulfate, potassium sulfate (in this case 1.26% of chloride as sodium chloride) and disodium phosphate are not sufficient to interfere with the use of the solubilities of the pure substances as a rough measure of the solubilities of the fertilizers themselves.

\*\* Van Nostrand—Chemical Annual, 1910.

until about January 15, when a lack of turgidity became noticeable, followed by a gradual stunting of growth, with the more pronounced signs appearing only after the middle of March. Signs of injury in sections treated in the same manner with sodium phosphate became evident even more slowly, while acid phosphate produced no apparent injury even in the largest applications.

The fertilizers may be grouped into the class, easily soluble and producing almost immediate injury; a second, moderately soluble and producing delayed injury; and a third, difficultly soluble and producing no apparent injury. On days of continuous sunlight a more or less pronounced softness of tissue could be detected by careful observation long before characteristic injuries became apparent.

**Effects of Overfeeding with Ammonium Sulfate.**—A marked softness of tissue was the earliest sign of overfeeding with ammonium sulfate. A complete plasmolysis took place in that portion of the stem located two and three nodes below the bud and in the portion of the stem just above the node, so that the stem bent completely over. The shoots first affected were those with buds one-half to three-quarters developed. At the same time white spots 0.25 and 1.00 mm. in diameter appeared upon the upper leaves of these and the younger shoots. Microscopic examination of these showed the chlorophyll bearing tissue entirely plasmolyzed.

In contrast to the injury from other fertilizers, practically every flower split.\* This splitting was not caused by the pressing outward of the petals as is usually the case, but by a weakening of the tissue at the line joining the sepals to form the calyx cup. Later stages resulted in the drying up of the leaf tips, and the appearance of the white depressions upon the older leaves. The sepal tips very early became brown. Later, pustule-like elevations about 1 mm. across appeared on them, caused by a crystal of ammonium sulfate beneath the epidermis. The injury from excess of ammonium sulfate was more rapid and pronounced in the presence of lime than without it.

**Effect of Overfeeding with Sodium Nitrate.**—Injury followed heavy applications of sodium nitrate within a few days, the characteristic symptom being an even lightening of color of the foliage over the plant, followed by drying of leaf tips and petals and withering of the plant.

**Effects from Large Applications of Sodium Chloride.\*\***—The first appearance of injury from large amounts of sodium chloride was two days after its application, a plasmolysis of the cells of the stem, causing it to lose its rigidity at the crown. When held within supports the plants appeared

\* Splits is a trade term denoting flowers with split calyces.

\*\* Sodium chloride, while not strictly a fertilizer, was used in the experiments because of its presence in considerable amounts in kainite and in some grades of commercial potassium sulfate.

normal. Gradually, however, the plants lost their turgidity and the chlorophyll disappeared evenly throughout the entire plant. Tests made in the spring of 1915 with heavy applications of sodium chloride and potassium chloride (12 kg. per 100 sq. ft.) showed the same effect from each of them, while sodium sulfate, like potassium sulfate, showed less injury and that only after a longer period.

**Effects of Overfeeding with Potassium Sulfate.**—In earlier stages partial wilting occurred on days of sunshine. Drying up of the tips of the leaves and curling of the leaves upward upon their long axis followed, with often, also, a peculiar inhibition of growth on one edge of the leaf, with the same on the opposite edge of another portion, giving the leaf a wavy outline.

A marked stunting of growth was observable. This affected most noticeably the lengthening of the stem, resulting in the later shoots assuming a rosette appearance, due to the leaves of normal length upon a stem with undeveloped internodes less than an inch in length. (The internode in full grown shoots is ordinarily three or four inches long.) The edges of the petals of the flowers after about the middle of January became quite generally withered or crinkled. Those in the center of the flower remained closed quite tightly, while the other two or three rows opened normally. Later, the buds remained closed, although the pistil often pushed its way out and might be seen extending an inch above the top of the bud.

A marked increase in exudation of nectar in the flower was found to have caused the gluing together of the petals, and so prevented their opening. On cloudy days very frequently a calyx cup would be found completely filled with this exudation. The exudation was most plentiful in the flowers from plants receiving a moderately heavy application of potassium sulfate over a long period of time while the heavier applications caused a noticeable but less plentiful increase. A small amount of nectar is found in normal flowers, and somewhat larger amounts in the flowers from plants receiving large applications of sodium phosphate, sodium chloride, ammonium sulfate, or potassium chloride, but not so generally nor in such large amounts as in the sections treated with potassium sulfate. Injury was less marked when ground limestone was added to the soil, in contrast to the effect of liming on the production of injury by ammonium sulfate.

**Effects of Overfeeding with Sodium Phosphate.**—When moderately large amounts of sodium phosphate were added over a long period (as in 1913-14) no injury was noticeable until about the middle of March, when a retardation of growth was evident from the decrease in height of the plants and abnormally small buds and flowers. These signs of inhibition became steadily more pronounced until the plants were removed from the

benches, about May first. When larger amounts were used (as 12 kg. per 100 sq. ft. in 1914-15), loss of turgidity in the plants, longitudinal rolling of the leaves, death of the leaf tips and softness of the petals of the blossom were evident. These signs of injury appeared, however, only after the middle of January and then only gradually. Injury was less when the soil was limed than when not.

**Effects of Overfeeding with Dried Blood.**—In none of the experiments with dried blood did injury appear until about the middle of January. At that time a softness of the petals and irregularity of their arrangement, due to the partial opening of the inner and crinkling of the outer ones, became more or less common. The flowers became susceptible to browning when a drop of water from syringing lodged on a petal in a position to be reached by the rays of the sun. The height of the plants was below normal in the spring but rather above in the fall; the color was good. If the applications of dried blood were not continued after signs of injury became apparent, the plants gradually recovered. The same held true for plants overfed with ammonium sulfate in contrast to those which had been injured by potassium sulfate, sodium phosphate, and sodium chloride.

**Effects of Overfeeding on the Mineral and Nitrogen Content of Plants.**

—Effects upon the dry weight and ash are shown in Table II, the samples being the foliage from the shoots gathered January 9, 1915.

TABLE II.—DRY WEIGHT AND ASH IN FOLIAGE.

Section No.	Treatment.	Moist weight.	Dry weight.	%.	Ash (sulfated) per cent. of dry weight.
269.	Check.	G. 27.6.	17.8.		13.68.
271	125 P*	32.4	17.6		13.93
273	250 P	32.2	18.3		12.89
275	500 P	30.6	18.9		14.28
277	125 K	26.1	18.4		15.37
279	250 K	36.8	20.4		15.45
281	500 K	32.8	22.6		15.59
283	Check	28.2	19.2		13.19
285	125 NaCl	42.9	22.8		14.45

The increase in both values as the applications of any one fertilizer in a series were increased is shown in the table. The higher values for plants treated with potassium sulfate and sodium chloride over those treated with sodium phosphate correspond to the higher osmotic pressure values obtained from the sap of these plants as well as to the more rapid injury from potassium sulfate.

Determination of the total nitrogen and mineral content of the ash

\* N, P and K in the tables are used to indicate ammonium sulfate, disodium phosphate and potassium sulfate, respectively, while NaCl indicates sodium chloride and A. P., commercial acid phosphate. The figures preceding the letters indicate the number of grams applied weekly per 20 sq. ft. of bench space.

from various samples of plants treated with potassium sulfate gave the following values:

TABLE III.—EFFECT OF POTASSIUM SULFATE.  
Analyses. Per cent.

Treatment.	$\text{Na}_2\text{O}$ .	$\text{K}_2\text{O}$ .	$\text{SO}_3$ .	N(total).	$\text{P}_2\text{O}_5$ .
Check	1.09	5.38	1.07	2.58	0.72
K	1.25	6.62	1.91	2.53	0.70
	0.16	1.24	0.84	—0.05	—0.02

The data show an increased sodium,\* potassium and sulfur content, with practically a constant percentage of nitrogen and phosphorus.

A similar study of plants to which ammonium sulfate had been applied gave the results shown in Table IV.

Plants to which sodium phosphate was applied showed a higher phosphorus content, 0.60%  $\text{P}_2\text{O}_5$  and 1.17%  $\text{P}_2\text{O}_5$  in a sample of 1915 in which the calcium content was decreased (2.31 and 1.63%  $\text{CaO}$ , respectively, in the last set of samples); the nitrogen content was increased by applications of sodium phosphate, the values 1.99%, 2.84% and 3.30% being obtained from plants to which had been applied, respectively, none, 250 g. and 500 g. of sodium phosphate per 20 sq. ft. of bench space per week for several weeks.

TABLE IV.—EFFECT OF AMMONIUM SULFATE.  
Analyses. Per cent.

Treatment.	N(total).	N(by $\text{MgO}$ ).	$\text{SO}_3$ .	$\text{P}_2\text{O}_5$ .
Check	2.05	0.168	0.75	0.93
N	2.93	0.364	2.10	1.14
	0.88	0.196	1.35	0.21

The ratio  $2\text{N}/\text{SO}_3$  in ammonium sulfate is  $28/80 = 0.351$ , that of total nitrogen to sulfur increase is 0.652; and of nitrogen by  $\text{MgO}$  0.145. The intake of sulfur when this fertilizer is used is less than is required for the nitrogen then, but in excess of that required to be combined with the nitrogen determined by  $\text{MgO}$ .\*\* Limestone was found to depress the sulfur intake from ammonium sulfate. Since injury was greater in sections so treated, the injury is not proportional to the intake of sulfur. The intake of phosphorus was increased by the addition of ammonium sulfate, probably due to acidity developed in the soil.

Table V shows the total nitrogen content of some plants from Sections 264 (ammonium sulfate and lime) and 281 (ammonium sulfate). Samples

\* Mayer<sup>22</sup> states that the addition of soluble potassium salts to a soil causes a partial replacement of the sodium.

\*\* The author would not care to report the presence of ammonium salts in plants not fed with it. It seems, rather, that  $\text{MgO}$  has caused some decomposition of the organic material; the error due to this is assumed to be the same in both samples.

were collected on April 25, 1914. Section 281 had received but one application at the rate of 12.5 kilos per 100 sq. ft. on December 3, 1913, while applications at the rate of 1250 g. per 100 sq. ft. were made to Section 264 at 15 different intervals of about two weeks after December 20, 1913. Analyses were made of upper and lower portions of the plant separately in order to show any localization of nitrogen in the more vigorously growing portion of the plant.

TABLE V.—TOTAL NITROGEN DETERMINATION ON FOLIAGE.

Sample No.	Plant No.	Section.	Portion.	Condition.	Nitrogen. %.
1	1	264-E	upper	half dead	4.58
2			lower	half dead	4.07
3	4	264-P	upper	half dead	7.78
4			lower	half dead	5.64
5	1	264-P	upper	dead	6.14
6			lower	dead	3.41
7	11	264-E	upper	alive	6.69
8			lower	alive	5.70
9	4	264-E	upper	half dead	7.01
10			lower	half dead	3.34
11	11-15	281-E	upper	dead	4.60
12			lower	dead	3.02
13	16	281-E	upper	partially affected	4.73
14			lower	partially affected	3.78
15	20	281-E	upper	half dead	4.73
16			lower	half dead	2.94
17	7	281-E	upper	slightly affected	4.47
18			lower	slightly affected	3.21

The total nitrogen content of the plants varied from once and a half to more than twice the normal value found in the previous set. Average values for the plants from Section 264 are 6.44% and 4.43%, respectively; for those from Section 281, 4.63% and 3.24%. In each case the more vigorously growing portion contained the larger percentage of nitrogen and the increase over the lower portion is considerably greater in the section to which the smaller applications were made during the entire season. No clear relation is shown between the nitrogen content and the degree of injury. Considerable tolerance for ammonium sulfate is shown when it was applied to the soil in quantities not heavy enough to produce immediate, serious injury. The fact that the dead plants had no higher total nitrogen content than those only injured is evidence that part of the nitrogen when added in small quantities was changed to a nontoxic form, since the dead plants were in this condition as early as March 21, while the living ones though injured undoubtedly continued to take up the salt in solution until samples were taken.

A series of ammonia determinations was made on the sap from "checks" and ammonium sulfate fed plants of the set of 12-9-14. Folin's micro-method for the determination of free<sup>14</sup> ammonia was used, the excess of

sulfuric acid (0.01550) being titrated back with potassium hydroxide 0.02130 with sodium alizarin sulfonate as the indicator. Results are given in Table VI.

TABLE VI.—FREE AMMONIA IN PLANT SAPS.\*

Sample No.	Treatment.	Appearance.	Nitrogen. Mg. N per cc.
5	check	normal	none
8	250 N	normal	0.1834
7	500 N	normal	0.1372
2	1000 N	slightly injured	0.6390
1	1000 N	badly injured	1.0560

The white spots on the leaves of plants treated with ammonium sulfate, and of crystals imbedded beneath the epidermis of the sepals were studied by microchemical methods.<sup>4</sup>

1. January 21, 1914. Plant Number 4, Section 281, White Enchantress. Plant apparently normal. A drop of sap from the stem of a shoot was treated with a drop of ammonia-free hydrochloric acid and chloroplatinic acid, and evaporated at room temperature under a loosely covering watch-glass. A few crystal masses, tetrahedral and often aggregated in shape of a cross, appeared. They were yellow in color. Sap from Number 8, somewhat injured, and Number 12, badly affected, gave these characteristic crystals, also.

2. A section of the leaf showing white blotches was immersed in chloroplatinic acid after removal of the epidermis and allowed to remain overnight. Large and perfect crystals appeared, arranged usually around the injured spot, never in it. They were insoluble in 95% alcohol which removed the excess of chloroplatinic acid.

3. A drop of sap from plant Number 4, Section 281 was distilled with a pinch of sodium carbonate over a micro-burner and the distillate caught in a hanging drop of hydrochloric acid in a cover glass placed on a glass ring above it. Treatment as above gave small, yellow tetrahedra insoluble in 95% alcohol.

Ammonium salts were evidently present and apparently caused plasmolysis of certain of the chlorophyll bearing cells. Why injury of this type is caused by ammonium sulfate in contrast to the even lightening of the color of the whole leaf by the other soluble salts, sodium nitrate and sodium chloride, is not known.

Nitrate determinations according to the phenolsulfonic method of Mason<sup>21</sup> were made upon the sap of a "check" and an ammonium sulfate fed plant from the set of March 9, 1915. The values of 0.01 and 0.40 mg. N as nitrate per cc. of sap, respectively, showed that nitrification was proceeding in the soil although it was quite strongly acid.<sup>17</sup>

\* In earlier stages of feeding with ammonium sulfate, samples have been taken in which no  $\text{NH}_3$  was detected by this method.

Total solids and ash were determined on the sap of the set of 12-9-14. The results, given in Table VII, are calculated to milligrams per cc. of sap.

TABLE VII.—TOTAL SOLIDS AND ASH OF SAP.

Sample No.	Set date.	Section.	Treatment.	Total solids. Mg. per cc.	Ash.* Mg. per cc.
2	12-9-14	291	1000 N	91.9	....
3		293	1000 K	104.9	19.2
5		289	check	63.8	11.8
6		261	check	62.1	12.1
7		265	250 N	63.6	13.9
8		267	500 N	79.9	15.1
9		277	125 K	64.3	16.1
10		279	250 K	69.9	17.2
11		281	500 K	75.7	17.1
12		283**	check	72.1	15.0
1	1-9-15	269	check	84.0	7.5
2		271	125 P	81.7	13.2
3		273	250 P	86.7	13.3
4		275	500 P	93.0	15.1
5		277	125 K	92.3	13.4
6		279	250 K	106.3	20.1
7		281	500 K	133.7	20.0
8		283**	check	105.1	14.1

The average total solids content of the sap was 85.1 mg. per cc. and the ash content 14.9 mg. The influence of the fertilizer applications is seen in the increase in both values as the applications of any fertilizer were increased in a series of sections. Sample 3 of the first set and 6 and 7 of the second, all of which were from plants to which large applications of potassium sulfate had been made, showed particularly high values.\*\*\* The first set of data was obtained by drying the samples in a Sargent electric oven at 60-70°, the second in a vacuum oven heated to 50° for 12 hours. The actual value for total solids depended on the length of heating but experiments with both sets of data given showed the same relative values after several successive heatings.

\* Ash determinations upon the sap were made by careful incineration of the solids in 1 cc. of sap in platinum dishes over a low flame to prevent mechanical loss of particles of the ash. The low chloride content obviates the danger of volatilization of potassium chloride by high temperatures.

\*\* For some reason total solids and ash determinations always ran higher in sap from plants in Section 283 than from those in other "check" sections. The same discrepancy is seen in the osmotic pressure data for these two sets.

\*\*\* The determination of total solids with accuracy is not possible on account of the uncrystallizable solutes in the sap, and on this account the mean molecular-weight calculations which often accompany osmotic pressure data were not made. Drying on the water bath was found to cause charring of the sap from plants which had been treated with ammonium or potassium sulfate. The first showed a higher acidity value, the second a higher sugar content.



Determinations of sodium and potassium in the ash from sap obtained on January 9, 1915, from plants treated with potassium sulfate, were made in order to show the increased intake of potassium. Similarly, determinations of phosphorus were made upon the sap from plants fertilized with disodium phosphate. The results, calculated to milligrams per cc. of sap, are given in Table VIII.

TABLE VIII.—MINERAL CONTENT OF SAP.

Sample No.	Section.	Treatment.	$\text{Na}_2\text{O}$ . Mg.	$\text{K}_2\text{O}$ . Mg.	$\text{Mg}_2\text{P}_2\text{O}_7$ . Mg.
9	277	125 K	1.4	9.4	...
10	279	250 K	1.3	10.1	...
11	281	500 K	1.3	10.1	...
12	283	check	1.2	8.4	...
1	269	check	...	....	1.5
2	271	125 P	...	....	6.1
3	273	250 P	...	....	7.5
4	275	500 P	...	....	9.6

**Effect of Overfeeding on Osmotic Pressure of Sap.**—Sap was expressed from the stems of shoots after freezing them with an ice-salt\* mixture, and the lowering of the freezing point determined by the method of Harris and Gortner\*\* of allowing supercooling until the solution froze and correcting the value of  $\Delta'$  obtained by the formula

$$\Delta = \Delta' - 0.0125 u \Delta'$$

where  $\Delta'$  is the maximum temperature attained in the system and  $u$  the difference between this value and the minimum temperature. The relation between  $\Delta$  and the osmotic pressure given by Lewis<sup>19</sup> in the approximate equation

$$\pi = 12.06 \Delta$$

was used in calculating the value for  $\pi$ .

**Description of Experimental Method.**—Choosing a time when for two or more hours previous no appreciable draft had been stirring the air in the greenhouse, from four to eight shoots at the same stage of growth were removed from each of the sections of plants and quickly taken to

\* Care was taken to select samples from the check and affected plants at the same time of day and shoots in the same stage of growth were taken, to insure freedom from variations in osmotic pressure due to differences in location and illumination, while the fact that the sections studied were usually adjacent obviated the difficulty that differences in temperature change the osmotic pressure of plants. See Dixon and Atkins,<sup>11</sup> Atkins,<sup>3</sup> Ewart,<sup>13</sup> Drabble and Drabble,<sup>12</sup> Cavara.<sup>8</sup>

\*\* The method in general was an adaptation of that recommended by Gortner and Harris.<sup>16-18</sup> André<sup>1</sup> and also Dixon and Atkins<sup>11</sup> have shown that successive portions of sap expressed from unfrozen tissue become more concentrated, while the latter have shown that the sap from frozen tissue always has a lower freezing point than that from unfrozen, and that successive portions gave nearly identical lowerings, leading to the conclusion that sap so expressed is representative of that originally within the tissue.

the laboratory. After removal of the foliage from the stems, they were broken at the nodes and placed in hard glass test tubes (25 mm.  $\times$  150 mm.), stoppered with rubber stoppers and sealed with oil paper and rubber bands. Freezing was produced by the use of the ice and salt bath,\* giving a temperature of  $-15^{\circ}$  or lower and allowing the tubes to remain in the refrigerator overnight. The tubes were then removed from the bath and after the walls had been cleaned with distilled water and wiped dry, the portions of shoots were removed, thawed gradually, and the sap expressed by pressure from the screw of a tincture press set perpendicular to the wall upon two pieces of  $\frac{3}{8}$  inch plate glass. After a first expression, the shoots were rearranged and pressure again applied. The sap was filtered through an S. & S. 589 filter—with a watch glass over the funnel to minimize evaporation—into a small test tube; a drop of xylene was added as a preservative and the tubes placed at once in a refrigerator, at about  $10^{\circ}$ . The sap after filtration was usually a clear, brown liquid without sediment.

As soon as convenient the freezing-point determinations were made. A thermometer was used having a bulb about 5 mm. by 35 mm., the mercury tube enclosed in a hollow jacket, and graduated to  $-6.5^{\circ}$  in tenths of degrees, upon which, by the aid of a lens, hundredths of a degree could be read without danger from parallax. A stirrer of platinum wire and the thermometer were placed in the 5 cc. of sap contained in a test tube of Bohemian glass (15  $\times$  120 mm.) and the whole cooled to about  $+2^{\circ}$  in an ice and salt bath in a beaker. The tube was wiped free from water and placed within a hard glass test tube (25 mm.  $\times$  150 mm.) set two-thirds way into the ice and salt-freezing mixture. It was found saving of time to place this bath in a Dewar bulb, with inside diameter of 35  $\times$  130 mm.; the top was closed with a piece of cork; the bath so arranged remaining effective for three hours or more of use. During the entire cooling, the sap was constantly stirred to prevent its freezing about the sides of the tube. The lowest temperature obtained was read to one-tenth, and the maximum, by the aid of a lens, to one-hundredth degree. The tube was removed to a beaker of water, and after the temperature had risen to about  $10^{\circ}$ , the determination duplicated to within  $0.01^{\circ}$ , usually without difficulty on the first trial. A typical determination gave the following values:

$$\begin{array}{lll} \Delta' = 1.28 & u = 4.12 & \Delta = 1.214 \\ \Delta' = 1.27 & u = 3.43 & \Delta = 1.216 \\ \text{Average } 1.215 \text{ from which } \pi = 14.64 \text{ atmospheres.} \end{array}$$

\* It was found convenient in case less than a dozen tubes of material were frozen, to place the ice and salt bath in one or two one-liter Jena beakers. In this way the ice can be packed about the upper portions of the test tubes, and the beakers, with five or six test tubes in them, are narrow enough to keep the tops of the test tubes from touching the solution.

TABLE IX.—OSMOTIC PRESSURE DETERMINATIONS.

Date.	Sample No.	Section.	Treatment.	$\Delta'$ .	$\kappa$ .	$\Delta$ .	$\pi$ .
11-12-15	1	291	1000 N	1.30	3.21	1.210	14.60
	2	293	1000 K	1.37	4.03	1.261	15.21
	3	295	1000 P	1.32	5.18	1.195	14.41
	4	289	check	1.15	3.90	1.054	12.71
	5	269	check	1.00	1.10	0.946	11.41
11-20-14	1	291	1000 N	1.33	5.67	1.196	14.42
	2	293	1000 K	1.50	3.40	1.396	16.84
	3	295	1000 P	1.10	4.80	0.994	11.99
	4	289	check	1.20	5.80	1.078	13.00
	5	283	check	1.18	2.87	1.098	13.24
	7	283	check	1.27	4.43	1.160	13.99
12-9-14 (10 A.M.)	1	291	1000 N	1.66	5.34	1.513	18.24
	2	291	1000 N	1.43	4.78	1.305	15.73
	3	293	1000 K	1.40	5.30	1.267	15.25
	5	289	check	0.95	4.55	0.856	10.34
	6	261	check	0.99	3.91	0.901	10.86
	7	265	250 N	1.10	5.10	0.990	11.94
	8	267	500 N	1.28	5.40	1.174	14.16
	9	277	125 K	1.05	3.75	0.962	11.60
12-9-14 (4 P.M.)	10	279	250 K	1.18	4.82	0.973	11.73
	11	281	500 K	1.18	4.32	1.076	13.01
	12	283	check	1.06	4.14	0.967	11.68
1-9-15	1	269	check	1.20	4.00	1.100	13.24
	2	271	125 P	1.28	4.62	1.169	14.08
	3	273	250 P	1.32	4.98	1.178	14.20
	4	275	500 P	1.39	3.81	1.284	15.50
	5	277	125 K	1.35	2.65	1.265	15.29
	6	279	250 K	1.58	4.92	1.448	17.49
	7	281	500 K	1.87	4.63	1.722	20.76
	8	283	check	1.28	4.92	1.161	14.04
	9	285	125 NaCl	1.88	2.92	1.771	21.40
	10	287	500 A. P.	1.48	5.52	1.338	16.13

**Discussion of Results.**—No comparison can be made between the values for the osmotic pressure determined in successive sets on account of variations due to temperature, physiological scarcity of water, etc., but the values obtained from plants in adjacent sections at the one time are regular enough to be comparable.

From the values for osmotic pressure of Samples 7, 8, 2 and 1 of the set of 12-9-14 the conclusion was drawn that the osmotic pressure within the plants increased as the quantity of ammonium sulfate applied to the soil was increased. Samples 2, 3 and 4, and 5, 6 and 7 of the set of 1-9-15 gave similar results with increasing applications of sodium phosphate and potassium sulfate. The values obtained from the application of sodium phosphate were in every case lower than those obtained from application of equal quantities of potassium sulfate or ammonium sulfate. The

samples taken on 11-12-14 and 11-20-14 gave higher values for the sap from plants overfed with potassium sulfate than those treated with ammonium sulfate, but later in the year in the set of 12-9-14 (Samples 1 and 2) the relative values are reversed.

In the set of 12-9-14 plants treated with potassium sulfate at the rate of 1000 g. per section per application were still apparently normal, although the osmotic pressure amounted to 15.25 atmospheres, while plants treated with one-half this weight of ammonium sulfate possessed an osmotic pressure of only 14.16 atmospheres and showed signs of injury. Injury, on the other hand, had not appeared on plants treated with ammonium sulfate (250 g. per section per application) when the osmotic pressure amounted to 12.42 atmospheres as compared to 11.34 atmospheres in the adjacent "check" section (12-9-14—10 A.M.).

The higher value of Sample 1 over Sample 2 (of the set of 12-9-14—10 A.M.) was correlated with a greater degree of injury by the ammonium sulfate. Injury appeared on the plants from sections to which potassium sulfate was applied, only when an osmotic pressure of over twenty atmospheres was reached (1-9-15), and an osmotic pressure value up to 15.50 atmospheres was found in plants on soil treated with sodium phosphate, without injury being apparent. The determination of the value on the sap from plants treated with acid phosphate gave 16.11 atmospheres, yet these plants exceeded in size and vigor those to which no fertilizer was applied (1-9-15). The conclusion to be drawn from these facts is that, with a single fertilizer, injury from overfeeding becomes apparent when a certain osmotic pressure is reached, but that this value is different for different fertilizers.

The injury from applications of sodium chloride at the rate of 125 g. per section per application, occurred at approximately the same time, was very similar to, and was of about the same degree as that from applications of potassium sulfate, in four times these quantities. The relative osmotic pressure values are given in Samples 9 and 10 (1-9-15). The solubilities of these salts, as pointed out on page 2785, at 0° are 35.7 and 8.5, respectively, giving a ratio roughly of 4 to 1.

**Effects of Overfeeding on the Total Acidity of the Cell Sap.**—Reaction tests with litmus paper showed that the soil receiving no fertilizer or only manure was neutral or slightly alkaline in the fall, and that a gradual change to slight acidity took place during the winter. Commercial acid phosphate, dried blood and ammonium sulfate upon the soil each increased the total acidity,\* the first one immediately after application,

\* It is not likely that the hydrogen-ion concentration of the soil solution was greatly increased by addition of commercial acid phosphate, since the formula used in its preparation prevents the presence of free sulfuric acid by providing a slight excess of tricalcium phosphate. Salm,<sup>23</sup> using a hydrogen electrode apparatus, found  $[H] = 3.3 \times 10^{-5}$  for the di-hydrogen sodium phosphate at 18° in 0.1 N sol.

the latter two within about a week's time. In the case of these fertilizers, the surface of the soil became acid after the lower portions. When disodium phosphate was applied, the surface of the soil became alkaline to litmus, the deeper parts becoming alkaline more slowly. Tests on Section 275 (500 P) on February 18, 1915, and on 291 (1000 P) on March 22, 1915, showed that the soil at each successive inch to the bottom of the bench, was alkaline to litmus. In so far as could be determined by this method, applications of potassium sulfate and of sodium chloride did not change the reaction of the soil.\* Hence an opportunity was given to study the effect, upon the acidity of the cell sap, of fertilizers producing increased acidity in the soil, alkalinity, and no change in reaction, and upon the relation the changes bore to injury from overfeeding with the fertilizer.

Determinations were made by titrating at about  $15^{\circ}$  with  $\text{CO}_2$ -free KOH, approximately 0.02 N, 1 cc. portions of sap diluted to 6 cc. with  $\text{CO}_2$ -free water, using phenolphthalein as the indicator. Results are calculated as cc. of normal acid per cc. sap.\*\*

TABLE X.—ACIDITY OF PLANT SAP.\*\*\*

Date.	Sample No.	Section.	Treatment.	Condition of plants.	Cc. N acid.
12-10-14	1	291	1000 N	affected	0.03068
	2	293	1000 K	normal	0.02492
	3	295	1000 P	normal	0.05490
	4	289	check	normal	0.02048
	5	261	check	normal	0.02090
	6	265	250 N	normal	0.02238
	7	267	500 N	affected	0.02728
	8	277	125 K	normal	0.02088
	9	279	250 K	normal	0.02002
	10	281	500 K	normal	0.02130
	11	283	check	normal	0.02130
1-14-15	12	269	check	normal	0.01977
	13	271	125 P	normal	0.05035
	14	273	250 P	normal	0.06438
	15	275	500 P	normal	0.07415
	16	277	125 K	normal	0.02319
	17	279	250 K	normal	0.02039
	18	281	500 K	affected	0.02422
	19	283	check	normal	0.02252
	20	285	125 NaCl	affected	0.01870
	21	287	500 A. P.	vigorous	0.06981

\* See, however, Maschaft.<sup>20</sup>

\*\* For memoir on acidity in plants, see Astruc.<sup>2</sup>

\*\*\* Boiling a solution of  $\text{CO}_2$  in distilled water under diminished pressure by warming the test tube with the hand was found completely to remove the  $\text{CO}_2$ . Similar treatment of sap gave identical values for acidity before and after. Hence, the acidity was not due to dissolved  $\text{CO}_2$ .

Acidity values remained about the same when potassium sulfate was applied, but increased after applications of acid phosphate, ammonium sulfate or disodium phosphate, being proportional in each case to the amount put on the soil. The increased total acidity following applications of disodium phosphate (which is alkaline to phenolphthalein) was unexpected and a more detailed study was made of the sap from these plants. Ether-soluble acids were absent and none of the phosphate was extracted by moisture-free ether. Phosphate was determined in 1 cc. portions of Samples 12-15 and the total acidity of the solution calculated on the assumption of the phosphorus being present (1) as orthophosphoric acid, and (2) mono-alkali phosphate,\* the values being given in Table XI.

TABLE XI.—ACIDITY OF SAP BY TITRATION AND CALCULATION.  
Acidity.

Sample No.	Treatment.	Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub> .	As H <sub>3</sub> PO <sub>4</sub> .	As XH <sub>2</sub> PO <sub>4</sub> .	By titration.
12	check	0.0015	0.02692	0.01346	0.01977
13	125 P	0.0061	0.10768	0.05384	0.05035
14	250 P	0.0075	0.13460	0.06730	0.06438
15	500 P	0.0096	0.16348	0.08174	0.07415

The values calculated as XH<sub>2</sub>PO<sub>4</sub> agree more closely than those for H<sub>3</sub>PO<sub>4</sub>, pointing to the presence of the phosphate as mono-alkali phosphates. Subtraction of the "check" value for Mg<sub>2</sub>P<sub>2</sub>O<sub>7</sub> from each of the other values to obtain the increase in phosphate intake due to applications of disodium phosphate and comparison of the titratable acidity calculated from these results with the excess of acidity of the solutions over that of the "check" gives the following results:

TABLE XII.—ACIDITY AND PHOSPHORUS CONTENT DUE TO OVERFEEDING.  
Increase in P<sub>2</sub>O<sub>5</sub>.

(1) As Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub> .	(2) As Mg <sub>2</sub> H.	(3) As Mg <sub>2</sub> H.	Ratio. (3)/(2).
0.0046	0.03999	0.03058	0.765
0.0060	0.05388	0.04461	0.827
0.0081	0.07276	0.05438	0.747

The ratio between the value of H determined by titration and by the gravimetric method at 15° was determined to be 0.905, so that the ratios obtained are in the same direction, although the lower values for the sap indicate that some of the phosphate may have been present as the mono-hydrogen phosphate.

This method was applied to the problem of determining the salt in form of which phosphorus enters the plants. In every case increasing applications of disodium phosphate gave higher acidity values. When brown rock phosphate was used (nasturtiums grown in sand culture with Hopkin's nutrient solution omitting phosphorus after the first application) a regular increase up to a maximum in size of plants followed by a

\* Two hydrogens of orthophosphoric acid and one of monosodium phosphate when the solution is concentrated at 0° and phenolphthalein is the indicator.\* At higher temperatures, hydrolysis of the salt increases the alkalinity of the solution.

decrease was obtained, without a consistent variation in the acidity of the sap. Rock phosphate fertilizer apparently is not taken into the plant as mono-calcium phosphate.

Reaction of the soil to litmus paper was determined from time to time. After the first applications of sodium phosphate the soil reacted alkaline to litmus on the surface, with decreasing alkalinity or acidity as the distance below the surface increased. On March 22, 1915, Section 295 (to which applications of 1000 g. of sodium phosphate had been made) was found to have an alkaline reaction to litmus paper when tested for each inch of soil down to the bottom of the bench (5 inches). Two shoots each from plant Number 4, badly injured, and plant Number 12, apparently normal, were taken and the sap expressed without previous freezing. The sap reacted acid to phenolphthalein in each case.

The power of soils to absorb bases from salts is well known.<sup>6</sup> With this in mind, a liter of solution of disodium phosphate was made up with carbon dioxide-free water, and aliquot portions titrated with standard sulfuric acid to a faint rose coloration, using phenolphthalein as the indicator. Six carnation cuttings, rooted in water, were cleansed by repeated washing with distilled water and floated on the surface of 500 cc. of the solution by placing them in holes of a paraffined cork. They were placed in the greenhouse for six days, covered with a large bell jar and shaded during the daytime. The cuttings were taken out, the solution carefully rinsed off and after removal of the roots the remainder of the shoots was frozen, the sap expressed, and 1 cc. portions titrated with standard alkali, using phenolphthalein as the indicator. Comparison was made with the acidity of the sap from cuttings taken from the cutting bench and prepared as in the former case for sap expression.

STRENGTH OF SOLUTION 2 G. $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ PER LITER.			
Titration of 10 cc. portions $\text{H}_2\text{SO}_4$ (0.01550 <i>N</i> ).		Titration of plant sap. KOH (0.02130 <i>N</i> ).	
(1).	(2).	(1) Check.	(2) Treated.
0.32 cc.	0.31 cc.	0.92 cc.	1.31 cc.
0.0048 cc. <i>N</i> alkali per cc.			

In the absence of soil, the sap had become more acid when the plants were grown in the disodium phosphate solution, hence the increased acidity could not be attributed, at least entirely, to the absorptive power of the soil for bases.

**Effect of Large Applications of Potassium Sulfate on Carbohydrate Content of Sap and Foliage.**—The increased exudation of nectar and gluing together of the petals in the flowers on plants which had been treated with large amounts of potassium sulfate has been listed among the characteristic signs of overfeeding with this fertilizer (page 2787). An attempt was made to determine the cause of this increased flow.

The amount of nectar present in an affected flower amounted to as much as 1 cc. in the spring of 1912-13, when applications of potassium sulfate,

moderate when compared with those used in 1914-15, were made weekly during the season October to May. In 1914-15 the flow was not so plentiful, although noticeably greater than in the "check" flowers. In the former year, the nectar was a brownish liquid with a sweet and bitter taste, miscible with water, while in the latter year it was a clear, colorless liquid. It had a sweet taste, and was neutral to litmus and phenolphthalein. It charred on ignition on a platinum foil, with the odor of burnt sugar, leaving a small amount of ash which was alkaline to moist litmus paper and to phenolphthalein. Sodium and potassium flame tests were positive, calcium doubtful. No indication of tannin was given by tests with neutral ferric chloride and with potassium ferricyanide and ammonia. A solution made by washing off the nectar with distilled water reduced Fehling's solution. A heavy osazone precipitate of bright yellow color was thrown down upon heating it in a boiling water bath with phenylhydrazine, acetic acid and a crystal of sodium acetate, after three minutes' boiling. Ten minutes' boiling increased the amount. A much heavier osazone precipitate was given after a few minutes' boiling with hydrochloric acid, and a portion of the solution inverted by the Clerget method gave a heavier osazone precipitate than a similar amount before inversion. The rotation in a 1 dm. tube of 1.5° Ventzke was changed to 1.18° V. after the Clerget inversion. Hence, glucose and sucrose were present. The precipitate formed in the hot solution was filtered off and the filtrate again boiled till no further precipitate separated. On cooling the filtrate a further precipitate of sodium acetate and osazone separated. This osazone possessed a roset structure characteristic of maltosazone, and was soluble in the boiling solution and reprecipitated from it on cooling as is maltosazone. Not enough of the precipitate could be obtained after recrystallization for a melting-point determination.\* Tests\*\* made with a guaiacol solution and neutral hydrogen peroxide gave a negative test with the exudation, but an equally intensive color with sections of petal, ovary, leaf and stem of both normal and affected plants. Neither of the reagents used alone gave a reaction. Microscopic examination of the lower, plasmolyzed portions of the petals showed the cell walls intact and of normal thickness. It was concluded from this that the increased amount of sugar was not due to breaking down of these cell walls, but was an exudation. Experiments were then undertaken to compare the sugar content of the sap expressed from the stems of the plants not fertilized and of those receiving applications of potassium sulfate. Evidence that a larger amount of sugars was present in the sap of the latter plants was

\* Brown and Morris<sup>4</sup> used 200 g. of leaf tissue in order to obtain enough for preparation of maltosazone.

\*\* Grüss<sup>18</sup> believed gummosis might be caused by an excess of diastatic enzyme, and used this reagent as a means of detecting it.



found during the determination of total solids of the sap (*vide supra*), when the residue from this sap was of greater weight and charred at a lower temperature than that of the check.

The comparative optical rotations\* and copper-reducing powers of sap from "check" sections and those which had received applications of potassium sulfate are shown in Table XV.

TABLE XV.—OPTICAL ROTATION AND CU-REDUCING POWER OF SAP SOLUTIONS.

Date.	Treatment	Rotation circ. degrees.			Reducing power. Mg. CuO.		
		Orig.	Hydrolyzed. <sup>e</sup>	Complete. <sup>f</sup>	Orig.	Clerget.	Complete.
1-9-15 <sup>a</sup>	check	0.73	0.83	....	....	....	....
	125 K	1.91	1.25	....	....	....	....
	250 K	1.42	0.97	....	....	....	....
	500 K	1.49	1.21	....	....	....	....
2-10-15 <sup>b</sup>	check	3.23	1.20 <sup>f</sup>	....	....	....	....
	K	3.51	1.35	....	....	....	....
2-17-15 <sup>c</sup>	check	2.81	1.53	0.67	556	1434	1654
	250-500 K	3.26	2.28	0.79	476.5	1461	1976
3-9-15 <sup>d</sup>	check	2.43	1.43	1.06	521	1276	(1282)
	250-500 K	3.00	1.91	1.34	522	1273	1438

In view of the work of Davis, Daish and Sawyer,<sup>9</sup> it seems possible, though not proven, that the quantitative relationships of the sugars in expressed sap may not represent the condition within the living tissue. The consistently higher values obtained by both methods of estimation, showed, however, that the application of potash to the soil had resulted in an increased carbohydrate production, in a more rapid hydrolysis of starch, or in a greater permeability of the cell membranes in the mesophyll tissue, so that a larger amount of sugar was found within the conducting and storage tissues.

Leaf tissue (Set 2-10-15) dried at 50-70° was extracted with 80% alcohol (1 g. pptd. CaCO<sub>3</sub> being added to neutralize acids present) and the extracts, after removal of alcohol, cleared with 5 cc. neutral lead acetate, 1 cc. basic lead acetate and alumina cream. The extracts from 7 g.

\* A. Schmidt and Häusch half-shadow polariscope, with tubes 4 dm. long, was used. CuO values were obtained by using Defren's<sup>10</sup> solution, the copper being determined by Low's method (Treadwell and Hall, p. 682).

<sup>a</sup> 5 cc. sap diluted to 50 cc. cleared with 5 cc. basic lead acetate (sp. gr. 1.115) and an excess of alumina cream.

<sup>b</sup> 20 cc. sap diluted to 100 cc. cleared with 10 cc. basic lead acetate and alumina cream.

<sup>c</sup> 10 cc. sap diluted to 100 cc. with 5 cc. basic lead acetate and alumina cream.

<sup>d</sup> 10 cc. sap diluted to 100 cc. with 2 cc. basic lead acetate and alumina cream.

<sup>e</sup> Hydrolyzed 24 hours with 10% 0.5 N HCl at 70°.

<sup>f</sup> Clerget inversion.

<sup>9</sup> Inversion for 3 hours in boiling water bath of 25 cc. soln 12½ cc. water and 2.5 cc. HCl sp. gr. 1.19.

made up to 100 cc. gave values shown in Table XVI. A trace only of pentoses was found in the extract.

TABLE XVI.—SUGAR DETERMINATIONS IN EXTRACTS.

Section.	Treatment.	Original.	Cupric-reducing power.	
			Mg. CuO.	
268-270	check	398.0	1656.8	1933.6
277	125 K	652.8	1873.6	1990.4

The results are similar to those in Table XV.

Examination was made for starch in carnation leaves taken from the plant after a day of sunshine by boiling them for some time in alcohol, then in water, and testing leaf sections with an alcoholic solution of iodine; starch was found to be plentiful. Comparative determinations of the starch content\* were made upon the residues from sugar extractions, using a diastase solution prepared by extraction of ground malt with mono-sodium phosphate solution at ice-box temperature, but not dialyzed.\*\* Fifty cubic centimeters of water were added to the residue and the starch gelatinized by boiling for five minutes, with continuous stirring. After cooling to 60°, 5 cc. of the diastase solution were added with a pipet and digestion allowed to proceed for an hour. The mixture was again heated to boiling and 5 cc. of diastase again added and after an hour the mixture was filtered and washed thoroughly. The maltose in the filtrate was hydrolyzed to glucose by the modified Sachsse method and glucose determined with Fehling's solution, correction being made for maltose in the diastase solution. The values obtained for samples from sets of 2-10-15 and 2-17-15 are shown in Table XVII.

TABLE XVII.—STARCH CONTENT OF CARNATION LEAVES.

Treatment.	Starch per cent.	
	2-10-15.	2-17-15.
check	2.72	3.44
K	1.94	3.09

A lower starch content in "check" tissue is indicated by the results. While these analyses were not made over a long enough period to form a basis for a conception of the effect produced by potash upon carbohydrate production and transformations, the higher sugar with lower starch content is interesting in view of the work of Sherman and Thomas<sup>24</sup> upon the activating action of potassium sulfate upon diastase.

### Summary.

The purpose of the investigation was to determine the effects upon the plants of large applications of certain commercial fertilizers to the soil on which carnations were grown.

\* Brown and Morris<sup>5</sup> state that preliminary washing with cold water as in the O'Sullivan method, is unnecessary in *Tropaeolum majus*.

\*\* Sherman and Schlesinger, *THIS JOURNAL*, 25, 1619 (1913).

The injuries characteristic of an excess of each fertilizer are recorded from observations made in the greenhouse.

Determinations of dry weight and ash made upon the foliage of the plants, showed an increase in both values with increased applications of the fertilizers.

A sufficient number of determinations of the mineral constituents of the foliage was made to show the increased content of the fertilizing salts in the plants after large applications of them to the soil.

Total nitrogen determinations made upon plants in different stages of injury showed an increased intake of nitrogen when ammonium sulfate was applied but an acquired tolerance by the plant when successive small applications were made. Injury from ammonium sulfate is not proportional to the total nitrogen content.

The sap was expressed from the stems of the plants after freezing to render the plasma membrane permeable to the contents of the cells. Osmotic pressure determinations made upon this sap proved that with each fertilizer used the degree of injury varied with the osmotic pressure, but that not the same degree of injury was caused by different fertilizers at the same osmotic pressure. Injury is not a result of increased osmotic pressure exclusively.

The increase in the osmotic pressure in a series of plants on soil receiving increasing applications of commercial fertilizers was accompanied by an increase in the total solids and ash of the sap and in the amount of the fertilizer taken up by the plant.

Determinations of total acidity showed an increase in the total acidity of the sap of plants fed with ammonium sulfate, disodium phosphate and monocalcium phosphate, when phenolphthalein was used as the indicator.

The relation between the increase in total acidity and in the phosphorus content of the sap when the plants were fed with disodium phosphate proved that the phosphorus was taken in the form of dihydrogen phosphate, due, as was shown, not entirely at least to absorption of the base by the soil but to the selective action of the plant. Applications of potassium sulfate had no effect upon the acidity of the sap.

The sap from the stems of plants grown on soil to which large applications of potassium sulfate had been made showed a higher total sugar content, the same results being obtained with extracts of foliage. The starch content of the foliage of such plants was lower. These data indicate a more rapid hydrolysis of the starch in the foliage in the presence of an excess of potassium sulfate. The increased exudation of nectar in the flowers of these plants probably resulted from this increase in sugar content.

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[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORY, THE UPJOHN COMPANY.]

## SOME CONSTITUENTS OF JAMBUL.

BY MERRILL C. HART AND FREDERICK W. HEYL.

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The Jambul Tree (*Syzygium Jambolana*), well known to the natives of the East Indies and Malay regions from China to New South Wales, for its edible fruit, is a large tree belonging to the *Myrtaceae*, sometimes attaining the height of ninety feet. A careful gleaner of the medical literature finds that three parts, the seed, pericarp and bark, have been employed in the treatment of *diabetes mellitus* with questionable results, but is perhaps impressed by some beneficent results reported. Two parts of the plant, the bark and the pericarp, have been recognized in the pharmacopeia of the Netherlands.<sup>1</sup>

The berry-like, sour fruit is about as large as the olive, and apparently forms a readily procurable commodity in the European market, whereas the term Jambul as used in this country refers to the flinty, hard seed contained in the pericarp. There is also some difference in opinion as to the part of the plant which should be employed in the manufacture of the fluid extract.

The early chemical studies showed the presence, in the bark, of tannin,<sup>2</sup> in the seed, of gallic acid.<sup>3</sup> The seed yields a trace of ethereal oil, 0.37% fat, and 0.3% resin, and pharmaceutical shrewdness, rather than chemical investigation, or conformance with a rational system of nomenclature, has given the name "antimellin" to an alleged glucosidic constituent.<sup>4</sup> This finding of Börsch could not be substantiated by Power and Callan.<sup>5</sup> The statement of Pottiez<sup>6</sup> concerning the presence of quercitol and cinnamic acid could not be confirmed by these chemists. Stephenson<sup>7</sup> found that the diastatic hydrolysis of starch was appreciably reduced by the presence of the extract of the fresh kernels.

Several preparations of German origin are marketed, *e. g.*, Djoeat, Bauers, Glykosolvol and Pavykol, which probably contain, in part, extracts from the bark or pericarps, and Djoeatin (Börsch) which is alleged to contain the above-mentioned "antimellin." The presence of tannin has recommended its use among the natives as an astringent, but on the whole, as stated in the Dispensatory, "it has failed to establish itself as a practical medicament."

The recent work of Power and Callan on Jambul seed, leaves the ques-

<sup>1</sup> *Ph. Nederl.*, IV.

<sup>2</sup> Johanson, Dissert., Dorpat, 1891.

<sup>3</sup> Elborne, *Pharm. J.*, 3, 932 (1888).

<sup>4</sup> Börsch, *Pharm. Ztg.*, 44, 574 (1899).

<sup>5</sup> *Pharm. J.*, 34, 414 (1912); 91, 245 (1913).

<sup>6</sup> *Ann. Pharm. Louvain*, 5, 373, 490 (1899).

<sup>7</sup> *Pharm. J.*, p. 211 (1892).

tion as to the pharmaceutical value of the pericarp. It was our plan to make a comparative study of the seed and pericarp, and we decided to investigate independently the seed, while awaiting a promised supply of pericarp, which unfortunately will not be available at present and we therefore report our work on the seed.

Our sample of Jambul seed, which was badly worm eaten, was received from Bombay. It was picked over and 91 pounds were rejected from a 200-pound shipment. The material contained 8.0% moisture and 2.9% ash. Ligroin extracted 1.2%, ether 1.3%, and alcohol 16.1%. The residue insoluble in alcohol had the following composition: crude fiber, 2.3%; pentosans, 2.1%; protein, 6.3%; starch, 41.4%; dextrin, 2.1%. The alcohol extract showed the presence of 0.3% sucrose and 3.3% reducing sugars. Tannin amounted to 6.0%.

The products present in the alcoholic percolate, and soluble in water, besides the sugars and tannin, are ellagic and gallic acids.

The study of the resin gave, in general, the same results as those reported by Power and Callan, *i. e.*, from the ligroin extract, oleic, linoleic, palmitic and stearic acids; from the ethyl acetate and alcoholic extracts, chiefly ellagic acid. We are, however, able to describe more fully the presence in the ligroin extract of myricyl alcohol, of a hydrocarbon very probably hentriacontane, and of a phytosterol,  $C_{27}H_{46}O$ , melting at  $135-135.5^{\circ}$  that formed an acetate, melting at  $119-120^{\circ}$ . The ether extract as well as the chloroform extract yielded in addition a phytosterolin,  $C_{33}H_{56}O_6$ , which we have described in detail.

We endeavored to repeat Stephenson's work which would indicate the presence of something in Jambul that would retard diastatic hydrolysis. In using the iodine method of Sherman, Kendall and Clark,<sup>1</sup> it was found to be impossible to read the end points of a diastatic hydrolysis because the presence of gallic acid in the extract decolorized the iodine solution. In the same way the reducing action of a Jambul extract is sufficiently great to render inaccurate their excellent gravimetric method employed for finding the activity of pancreatin.

### Experimental.

(A) **Proximate Analysis.**—A sample of the air-dried seed after grinding and sieving was quantitatively extracted with various solvents, with the following results:

Extract.	Per cent.
Ligroin (35-55°).....	1.2
Volatile ether extract.....	0.2
Ether.....	1.3
Alcoholic.....	16.1

The proximate analyses were conducted in accordance with the usual methods, and gave the result tabulated below:

<sup>1</sup> THIS JOURNAL, 32, 1073 (1910).

	Per cent.		Per cent.
Moisture.....	8.0	Protein.....	6.3
Starch (diastase).....	41.4, 40.3	Ash.....	2.9
Crude fiber.....	2.3	Dextrin.....	2.1
Pentosans.....	2.1	Tannin <sup>1</sup> .....	6.0

The quantitative examination of the alcohol-soluble carbohydrates resulted as follows:

100 g. of Jambul seeds were extracted with boiling 95% alcohol. The alcoholic extract was concentrated to a syrup, precipitated with a slight excess of lead subacetate and made to a volume of 200 cc. The direct and invert readings at 22° in 2 dcm. tube are —2.6V, and 3.2V, respectively. The invert reading at 86° in a 2 dcm. tube was 0.35V. Hence sucrose = 0.23%, fructose = 2.3%, and glucose = 2.1%, respectively. Gravimetric determinations by the Walker-Munson process gave sucrose 0.33% and reducing sugar 3.3%.

(B) **Examination of Alcoholic Extract.**—For this purpose 45.4 kg. were exhausted by percolation with wood alcohol at room temperatures. Power and Callan extracted the seed with hot ethyl alcohol. The percolate (397 l.) was concentrated under diminished pressure to a volume of 12.5 liters. This concentrated extract on standing deposited 230 g. of yellowish material which was quite insoluble in the usual organic solvents. It could be redissolved in dilute alkali and then reprecipitated by the addition of acetic acid. After being digested with ether, and with ethyl acetate, this material was crystallized from pyridine. Brown needles were obtained that gave the characteristic tests for ellagic acid.

The filtered alcoholic extract was poured into 25 l. of distilled water and vigorously agitated. After long standing the resin was removed by filtration. The aqueous alcoholic filtrate was concentrated under reduced pressure in order to remove the alcohol. When this solution was diluted with distilled water, further precipitation took place even after diluting to a volume of 80 liters. The solution was allowed to stand overnight and the precipitate (372 g.) was filtered off. This material was of the nature of a phlobaphene. The filtrate was concentrated to a volume of 9.77 l. It now deposited 84 g. of ellagic acid. This deposit was digested with ether and with ethyl acetate and crystallized three times from pyridine. The crystals were washed successively with water, ethyl acetate and ether, dried at 150° and analyzed.

Calc. for  $C_{14}H_6O_8$ : C, 55.6; H, 2.0 Found: C, 55.6; H, 2.1.

The aqueous solution containing 5276 g. of water-soluble plant extractive was divided and a quantity containing 3750 g. was extracted repeatedly with large volumes of ether, which extracted 524 g. of a greenish white solid, which proved to be gallic acid. This amounts to 1.63% of the drug. A portion of this crude gallic acid was digested with fresh ether, which removed the color. The residue crystallized from water in colorless

<sup>1</sup> Both the Hide powder method, and the Proctor-Lowenthal method gave the same results.

needles, decomposing at about  $240^{\circ}$ . It was dried at  $115^{\circ}$  and identified as gallic acid:

Calc. for  $C_7H_6O_5$ : C, 49.4; H, 3.5. Found: C, 49.4; H, 3.4.

The dark green ethereal filtrate from the purified gallic acid was exhaustively examined, and a small quantity of sulfur melting at  $114-115^{\circ}$  was identified as a constituent.

The aqueous solution which had been completely extracted with ether, was now extracted with chloroform, which extracted only 3 g. of material. This was redissolved in chloroform and fractionally extracted with the usual alkaline solvents which yielded nothing definite. The neutral solution upon evaporation yielded a minute quantity of crystalline material melting at  $115-121^{\circ}$ . This gave the color tests of the phytosterol group.

The aqueous solution which had been completely extracted with ether and chloroform was now extracted repeatedly with hot amyl alcohol. During this extraction there ensued a gradual precipitation of ellagic acid. The material extracted with amyl alcohol weighed 742 g., equivalent to 2.2% of the drug. This extract contains a considerable quantity of ellagic acid. The amyl alcoholic extract could be prepared as a greyish white powder, by precipitation with petroleic ether. From dilute alcohol and from pyridine solutions, ellagic acid separated. A part (58 g.) of the amyl alcoholic extract was redissolved in this solvent and the solution was extracted with the usual alkaline solvents, but nothing crystalline was separated by this procedure. Another part (127 g.) was hydrolyzed by boiling for several hours in the presence of 5% sulfuric acid, but no crystalline hydrolytic products were found. Eighty-four grams were hydrolyzed by boiling for one minute with 10% potassium hydroxide solution. The mixture was cooled and poured into an excess of dilute sulfuric acid, and then steam distilled. From the contents of the flask a quantity of gallic acid, melting at  $240-242^{\circ}$ , was isolated.

A quantity (171 g.) was boiled with a large volume of water and then vigorously steam distilled. Ellagic acid separated. The solution was concentrated and further quantities of ellagic acid separated. At length, after evaporation to dryness, the residue was boiled with ethyl acetate and some insoluble material (ellagic acid) was removed by filtration. It was impossible to obtain crystals from this solution. The ethyl acetate solution was evaporated to dryness, and again taken up in dry ethyl acetate, in which it was freely soluble, but nothing definite could be obtained from it. The amyl alcoholic extract is not glucosidic.

The aqueous liquid which had been extracted with ether, chloroform, and with amyl alcohol, was freed from the latter immiscible solvent by a vigorous steam distillation. The distribution of nitrogen in this solution was as follows: Total soluble nitrogen, 0.0649%; ammonia nitrogen, 0.0079%; lead subacetate precipitable nitrogen, 0.0197%.



In order to test for acid amides, one-fifth of the solution was precipitated with mercuric acetate solution, but the results were negative.

The remainder of the solution was precipitated with basic lead acetate, filtered, and the precipitate was found to consist essentially of lead tannate.

The filtrate from the lead tannate was freed from lead with hydrogen sulfide and sharply concentrated. Although this syrup yields a precipitate with phosphotungstic acid, no nitrogenous bases were isolated from this fraction. The only product found was sugar, a crystalline deposit of a *d*-phenylglucosazone melting at 207–208° being readily prepared. Pentose sugars were absent.

**The Examination of the Resin.**—The resin which precipitated when the alcoholic extract was poured into water weighed about 699 g., equivalent to 1.5% of the drug. It was dissolved in wood alcohol, poured upon purified sawdust, transferred to a continuous extractor, and extracted with the following results:

Ligroin (40–60°).....	433 g.
Ether.....	20
Chloroform.....	13
Ethyl acetate.....	79
Alcohol.....	109

---

Total, 654 g.

**The Ligroin Extract.**—Three hundred grams were dissolved in ether and shaken with solutions of potassium hydroxide (5% and 10%). The alkaline extractions were acidified and extracted with ether. This ethereal solution was successfully extracted with a solution of ammonium carbonate (10%) but these extracts yielded nothing but a small quantity of smeary material precipitable with acid.

The ethereal solution was now extracted with solutions of potassium carbonate, and the fatty acids occurring free in the plant were removed. The alkaline extract containing the potassium salts of these fatty acids was acidified and extracted with ether. The ethereal solution of fatty acids was dried over anhydrous sodium sulfate. The ether was removed and a residue of about 92 g. obtained. This was distilled under diminished pressure. The boiling point was 215–250° at 20 mm., and the iodine number of the distilled acids which solidified in the receiving tube was found to be 88.7. A very considerable quantity of this material could not be distilled and it remained as a tar in the flask. These fatty acids were studied in connection with those obtained upon the subsequent hydrolysis of the glycerides.

The ether solution which had been extracted with ammonium carbonate and potassium carbonate was now extracted with a solution of potassium hydroxide. The alkaline extract was acidified and a quantity

of tarry material (15 g.) precipitated. This was dissolved in alcohol and subjected to acid and alkaline hydrolysis, but nothing crystalline could be separated in either case.

The ether solution which had been extracted with solutions of ammonium carbonate, potassium carbonate and potassium hydroxide contained 17 g. of neutral material belonging to the unsaponifiable material. It boiled at 120–250° at 15 mm., and yielded oily distillates exactly corresponding to those described among the unsaponifiable products of the fat.

The original ethereal solution of the fat which had been extracted with solutions of potassium hydroxide was evaporated to dryness and the residue was saponified by boiling with 250 cc. of 10% alcoholic potash for about five hours. The alcohol was removed and water added to completely precipitate the unsaponifiable material, which was extracted with ether.

**Examination of the Unsaponifiable Matter.**—The dried solution was evaporated to dryness and the residue was an orange-colored oil amounting to 47 g. It was dissolved in absolute alcohol and upon standing 0.15 g. of material separated. The melting point was indefinite (62–76°) and suggested, as stated by Power and Callan, a mixture of hydrocarbon and a higher alcohol. By means of the phthalic acid fusion, and subsequent extraction with sodium carbonate, a small quantity of a hydrocarbon melting at 61° was isolated. Three crystallizations from ethyl acetate raised this melting point to 63°. It separated in colorless leaflets and was perhaps impure hentriacontane.

Calc. for  $C_{31}H_{64}$ : C, 85.3; H, 14.7. Found: C, 85.1; H, 14.1.

A small quantity of a sodium salt of an acid phthalic ester was isolated and boiled with alcoholic potash. A product separated which had the melting point of myricyl alcohol, 82–84°. It crystallized from alcohol in leaflets, which softened at 82° and melted at 85°.

Calc. for  $C_{30}H_{62}O$ : C, 82.2; H, 14.1. Found: C, 81.7; H, 13.5.

The alcoholic solution from which the hydrocarbon and myricyl alcohol had separated yielded no further crystallizations even from concentrated solutions after the addition of small quantities of water. This residue was distilled under diminished pressure.

Fraction I (b. p. 120–160° at 10 mm.). This was a colorless, limpid oil with a fragrant odor. The weight was 11 g.

Fraction II (b. p. 160–200° at 10 mm.). This was a colorless oil, less mobile than the first fraction, and of about the same weight. A systematic fractional distillation of I and II effected no separations.

Fraction III (b. p. 200–250° at 10 mm.). This was a thick viscid oil which partially solidified. It weighed about 5 g.

The fractions collected above 250° at 10 mm. solidified in the receiver. The fraction boiling at 280–340° at 10 mm. was crystallized from ethyl

acetate. The material melted at about  $132^{\circ}$ , but softened somewhat lower. It was necessary to separate a small quantity of low-melting material ( $70-75^{\circ}$ ) by a fractional crystallization and phytosterol then separated in glistening plates, melting sharply at  $135-135.5^{\circ}$ .

Calc. for  $C_{27}H_{46}O.H_2O$ :  $H_2O$ , 4.5. Found: 5.6%.

Calc. for  $C_{27}H_{46}O$ : C, 83.9; H, 11.9. Found: C, 83.8; H, 11.6.

0.1163 g. of the anhydrous phytosterol made up to 20 cc. with chloroform showed a rotation of  $-0.489$  in a 2 dcm. tube, whence  $[\alpha]_D^{25} = -42.04^{\circ}$ .

It yielded an acetyl derivative that separated from acetic anhydride in thin plates which melted at  $119-120^{\circ}$ .

**Examination of the Fatty Acids.**—The alkaline solution from which the unsaponifiable matter had been extracted with ether was acidified and the liberated fatty acids were extracted with ether. The ether solution was dried over anhydrous sodium sulfate, concentrated to a small volume and then largely diluted with ligroin which precipitated some tarry material. This was removed by filtration, and the solvent was distilled from the fatty acids. These boiled chiefly at  $230-260^{\circ}$  at 15–20 mm. A small fraction distilled at  $260-280^{\circ}$  at 20 mm. The weight of distilled acids was 30.1 g., and the iodine number was 98.3.

These acids were mixed with those which had been extracted with potassium carbonate solution. A portion weighing 22.5 g. was converted into the lead salts, which were treated with ether. The liquid acids obtained from the lead salts soluble in ether weighed 12.9 g. (57.3%). These boiled chiefly at  $235-245^{\circ}$  at 32–34 mm.

Calc. for  $C_{18}H_{34}O_2$ : C, 76.6; H, 12.1; iodine no., 90.1; for  $C_{18}H_{32}O_2$ : C, 77.1; H, 11.4; iodine no., 181.4. Found: C, 76.6; 76.7; H, 11.3, 11.55; iodine no., 131.7.

The liquid acids therefore consist of a mixture of oleic and linoleic acids.

The lead salts of the fatty acids, insoluble in ether, were decomposed with hydrochloric acid and the solid fatty acids separated in the usual manner. When dissolved in absolute alcohol with the object of separating any of the more insoluble acids by crystallization, it was found that the acids were very readily soluble and no satisfactory crystallization could be obtained even from very concentrated solutions. The alcoholic solution was fractionally precipitated with an alcoholic solution of barium acetate. This yielded Fractions I and II. Fraction III was precipitated by the addition of water.

1. Melting at  $51-53^{\circ}$ . C, 75.8; H, 12.4; N. v., 204.3.

III. This fraction was an oil and gave entirely anomalous analytical data. Iodine no., 35.2, 34.7; neutralization value, 34.9; and saponification value, 140.2.

The solid acids are therefore a mixture of palmitic and stearic acids.

Calc. for  $C_{16}H_{22}O_2$ : C, 75.0; H, 12.5; N. v., 219.1.  $C_{18}H_{26}O_2$ : C, 76.1; H, 12.7; N. v., 197.5.

**The Ether Extract of the Resin**, which amounted to 20 g., contained a quantity (2 g.) of an insoluble white solid. This was filtered off. When this substance was dissolved in chloroform, in the presence of a few drops of acetic anhydride, and sulfuric acid was added, a play of colors resulted showing at first transient pink; then blue, and finally a beautiful green. It was crystallized several times from dilute pyridine, and then melted at  $275-285^\circ$ . It was a phytosterolin. After being dried to constant weight at  $120^\circ$  it was analyzed.

Calc. for  $C_{33}H_{50}O_6$ : C, 72.3; H, 10.2. Found: C, 72.3; H, 10.2.

A portion of this was converted into an acetate, which crystallized from dilute alcohol in colorless, glistening leaflets melting at  $167-168^\circ$ .

0.5036 g. of the anhydrous phytosterolin acetate, when made up to 20 cc. with chloroform, showed a rotation of  $-1.21^\circ$  in a 2 dcm. tube, whence  $[\alpha]_D^{23} = -24.1$ .

One gram of this phytosterolin was hydrolyzed according to the method outlined by Power and Salway.<sup>1</sup> It was dissolved in 60 cc. of hot amyl alcohol and 20 cc. of an aqueous 15% solution of hydrochloric acid added, together with sufficient ethyl alcohol to form a homogeneous liquid. After heating for three hours in a reflux apparatus, steam was passed through the mixture to remove the amyl alcohol, and the contents of the flask then filtered. A solid substance was thus collected, which after several crystallizations from ethyl acetate, alcohol, and dilute alcohol, separated in glistening leaflets melting at  $134-135^\circ$ . The mother liquors from this crystallization contained a relatively large quantity of an oily resinous material which had evidently been formed from the phytosterolin by too prolonged hydrolysis. The crystals gave the phytosterol color reaction.

0.0983 g. made up to 20 cc. with chloroform had a rotation of  $0.38^\circ$  in a 2 dcm. tube, whence  $[\alpha]_D^{25} = -38.8$ .

Calc. for  $C_{27}H_{46}O$ : C, 83.9; H, 11.9. Found: C, 83.3; H, 11.3.

The acid aqueous liquid, from which the phytosterol had been separated by filtration, was exactly neutralized with sodium carbonate, evaporated to dryness, the residue digested with absolute alcohol, and the mixture filtered. On evaporating the alcoholic filtrate a small amount of syrupy residue was obtained, which reduced Fehling's solution, and yielded an osazone melting and decomposing at  $212^\circ$ . It was thus evident that the sugar was glucose.

Thus this phytosterolin is shown to be phytosterol-*d*-glucoside.

The ether extract from which the phytosterolin had been separated was fractionally extracted with varying strengths of alkali. The potas-

<sup>1</sup> *J. Chem. Soc.*, 103, 399 (1913).

sium hydroxide extracts removed practically all the dissolved matter as a green oil which after some time became semi-solid. This could not be crystallized and was unchanged when boiled for several hours in the presence of an alcoholic solution of 5% sulfuric acid solution.

**The Chloroform Extract of the Resin** weighed 13 g. Part of this extract was quite insoluble in ethyl acetate and alcohol with which it was digested. This part was crystallized twice from dilute pyridine and melted at 280–295°. This gave the usual color test for a phytosterolin. After crystallization it weighed 3 g. Altogether the phytosterolin isolated from the ether and chloroform extracts amounted to 5 g. or 0.011% of the air-dried drug.

The filtrate from the above phytosterolin was evaporated to dryness, taken up in chloroform, and then fractionally extracted with varying strengths of alkali. Nothing of a crystalline nature was obtained by this procedure.

**The Ethyl Acetate Extract of the Resin** was a mixture of ellagic acid and tannin-like substances. Upon distilling off a portion of the ethyl acetate about half of it separated as crude ellagic acid, which when crystallized once from alcohol yielded 13 g. of pure acid that did not melt at 350°. The mother liquor from this separation was a smear, that colored ferric chloride solution black, and precipitated a gelatin solution.

The part soluble in ethyl acetate was thoroughly examined but nothing was isolated.

**The Alcoholic Extract of the Resin** yielded 15 g. further of ellagic acid. The total ellagic acid separated amounts to 1.2% of the plant. Neither an acid hydrolysis or a potash fusion gave any interesting decomposition products. Neither the ethyl acetate fraction nor the alcoholic extract was glucosidic.

KALAMAZOO, MICH.

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## NEW BOOKS.

**Laboratory Manual of Inorganic Chemistry for Colleges.** By LYMAN C. NEWELL, Ph.D., Professor of Chemistry, Boston University. Boston: D. C. Heath & Co. Pp. vi + 240.

Although this book is prepared primarily to be used as a laboratory guide in connection with the author's "Inorganic Chemistry for Colleges," the experiments are of such a nature and scope that it could be used advantageously with any standard text. The directions for the experiments are clear and definite, and are based on the author's long experience as a laboratory teacher. A large number of experiments of graded difficulty are given, and provision is thus made for students of widely different preparation in chemistry. The apparatus required for most of the work is simple and inexpensive. The book appears to be one that

could be used profitably in a large laboratory where students are unable to have the directions for the experiments frequently interpreted by an instructor.

JAMES F. NORRIS.

**Elementary Qualitative Analysis.** By BENTON DALES, Professor of Chemistry, University of Nebraska, and OSCAR LEONARD BARNEBY, Instructor of Chemistry, University of Wisconsin. Pp. 206. John Wiley and Sons, N. Y.

True to title, this book contains little theory, few novelties in methods, no rare elements or unusual compounds. That the student may learn to work understandingly, that he may see the reasons for the processes he uses and become able to devise simple methods of separation, are ends apparently held as important as analytical results.

The first half of the book aims to extend the student's knowledge of general chemistry, particularly as to those facts on which the qualitative scheme is based. The first 25 pages are devoted to the ionic theory, equilibrium, nomenclature, reactions and equations, a treatment too condensed to give true ideas of these subjects to one meeting them for the first time. Apparently no use of the ionic theory or equilibrium is subsequently made. For example, the double salt theory is used to explain the non-precipitation of such compounds as manganese and magnesium hydroxides by ammonia in the presence of ammonium chloride.

About 70 pages are occupied by statements of properties and reactions of acids and bases, which the student is expected to verify experimentally. This is excellent, perhaps too extensive for an elementary course. Here and throughout the book are many lists of well selected questions. If the student is held rigidly to this work and to the questions, he can scarcely fail to secure a large amount of knowledge of analytical methods before he reaches the formal scheme for the analysis of "unknowns." His work can hardly become mechanical thereafter. It would probably increase his interest, give point to the testing and help to fix the facts in mind, if, instead of first working through the whole 70 pages, he were permitted after testing through a group of metals to take up the separation of that group.

Another good feature is a list of reagents in which concentration is given in terms of normality and the corresponding number of grams per liter. Yet another is a chapter on short processes and deductions, based on a table of solubilities and the properties studied in the general testing. This should appeal to the student as a time-saver and also prevent mechanical habits.

W. S. HENDRIXSON.

# Author Index to Volume XXXVIII, 1916.

ACREE, S. F.	Constituents of poison ivy, 1421; see Brown, B. M.; Loomis, N. E.; Lubs, H. A.; Taylor, W. A.	
ADAMS, E. Q.	Relations between constants of dibasic acids and amphoteric electrolytes.....	1503
ADAMS, R. AND BEEBE, C. H.	Action of the Grignard reagent on CN compds.—synthesis of amidines from cyanamides.....	2768
ADAMS, R. AND WEEKS, L. F.	Action of oxalyl chloride on primary, secondary and tertiary alcohols.....	2514
AITCHISON, L.	See Ibbotson, F.	
ALDRICH, T. B. AND BECKWITH, C. P.	Derivs. of trihalogentertiary-butyl-alcohols (I) acetic ester of tribromotertiary-butyl-alcohol or brometone acetic ester.....	2740
ANDEREGG, F. O.	See Richards, T. W.	
ANDREWS, C. E.	See Boehner, R. S.	
ARRHENIUS, S.	Quant. Laws in Biological Chemistry (book rev.).....	939
AVERITT, S. D.	See Blumenthal, P. L.	
BAILEY, G. C.	See Johnson, T. B.	
BAILEY, J. R. AND McPHERSON, A. T.	5,5-Dimethyl-3-R-2-thiohydantoin.....	2523
BAILEY, J. R. AND MIKESKA, L. A.	Hydrazino diacids.....	1771
BAKER, J. C.	See Sherman, H. C.	
BALKE, C. W.	See Hopkins, B. S.	
BALY, E. C. C.	Theory of chem. reaction and reactivity.....	15, 227
BARAB, J.	See Cope, W. C.; Neidle, M.	
BARNEBY, O. L.	Differential iodimetry—detn. of periodates, iodates, bromates and chlorates in presence of each other, 330; bath used for soln. of samples in O-free atm.....	374
BARTLELL, F. E. AND HOCKER, C. D.	Relation of osmose of solns. of electrolytes to membrane potentials—theoretical, 1029; osmose of some solns. of electrolytes with porcelain membranes, and relation of osmose to membrane potential.....	1036
BATES, J. S.	See Johnson, T. B.	
BAXTER, G. P.	23rd ann. rept. on at. wts.—detns. published during 1915.....	489
BAXTER, G. P. AND GROSE, M. R.	Revision of at. wt. of Zn—electrolytic detn. of Zn in ZnBr <sub>2</sub> ..	868
BAXTER, G. P., GROSE, M. R. AND HARTMANN, M. L.	Revision of at. wt. of Cd (IV) electrolytic detn. of Cd in CdBr <sub>2</sub> .....	857
BAXTER, G. P. AND HAWKINS, C. F.	Densities and cubical coeffs. of expansion of As <sub>2</sub> O <sub>3</sub> , PbCl <sub>2</sub> , PbBr <sub>2</sub> , NdCl <sub>3</sub> .....	266
BAXTER, G. P. AND STARKWEATHER, H. W.	Efficiency of CaCl <sub>2</sub> , NaOH and KOH as drying agents.....	2038
BAXTER, G. P. AND WALLACE, C. C.	Changes in vol. on soln. in water of halogen salts of alkali metals (II), 70; densities and cubical coeffs. of expansion of halogen salts of Na, K, Rb and Cs.....	259
BAXTER, G. P., WHITCOMB, W. H., STEWART, O. J. AND CHAPIN, H. C.	Revision of at. wt. of Nd (II).....	302
BEAL, G. D. AND MUNCIE, F. W.	Effects of large applications of commercial fertilizers on carnations.....	2784
BECKWITH, C. P.	See Aldrich, T. B.	
BEEBE, C. H.	See Adams, R.	
BEGGS, S. A.	See Jackson, C. L.	
BELL, J. M.	Free energy and heat capacity.....	2629
BICHOWSKY, F. R. v.	See Randall, M.	
BIDDLE, H. C.	Rates of conversion of stereoisomeric cinchona alkaloids into their toxins....	901
BILECKI, A.	Ueber das periodische System der chemischen Elemente (book rev.).....	732
BINGHAM, E. C., SCHLESINGER, H. I. AND COLEMAN, A. B.	Sources of error in viscosity measurement.....	27
BISSELL, D. W.	See Derick, C. G.	
BISSELL, D. W. AND JAMES, C.	Gadolinium sodium sulfate.....	873
BLAKE, J. C.	Digestibility of bread (I)—Salivary digestion <i>in vitro</i> .....	1245
BLUM, W.	Detn. of Al as oxide.....	1282
BLUMENTHAL, P. L. AND AVERITT, S. D.	Estn. of thiosulfate S in lime-S solns. by I titration.	1701
BOEHNER, R. S. AND ANDREWS, C. E.	Pyrogenetic decompn. of amides.....	2503, 2505
BOBERT, M. T. AND SCATCHARD, G.	Quinazolines (XXXIII) new and sensitive indicator for acidimetry and alkalimetry, and for detn. of H-ion concns. between limits of 6 and 8 on the Sorensen scale.....	1606

- BOGERT, M. T. AND TUTTLE, J. R. Synthesis of *p*-cymene 2-monocarboxylic acid and of *p*-cymene 3-monocarboxylic acid, together with certain of their derivs. .... 1349, 1904
- BONCQUET, P. A. Presence of nitrites and  $\text{NH}_3$  in diseased plants—its significance with regard to crop rotation and soil depletion ..... 2572
- BOND, P. A. See Karslake, W. J.
- BOOGE, J. E. See Kendall, J.
- BOVARD, W. M. See Vinal, G. W.
- BOWERS, W. G. See Hillebrand, J. H.
- BRANCH, G. E. K. Hydrolysis of hexahydropyrimidine ..... 2466
- BRANN, A. See Walton, J. H.
- BRAUNS, D. H. See Hudson, C. S.
- BREWSTER, R. Q. See Dains, F. B.
- BRIDGMAN, P. W. Black P. .... 609
- BRINTON, P. H. M.-P. Be vanadates ..... 2361
- BROOKS, B. T. Zingiberol, new sesquiterpene alc. in essential oil of ginger, 430; see Risse, H.
- BROOKS, B. T. AND HUMPHREY, I. W. Presence of benzene homologs in the high boiling distillates of petroleum ..... 393
- BROWN, B. M. AND ACRHE, S. F. Catalysis (XXIV) reaction of both the ions and nonionized forms of acids, bases and salts: reaction of  $\text{MeI}$  with  $\text{Na}$ ,  $\text{K}$  and  $\text{Li}$  ethylates at  $0^\circ$  .... 2145
- BROWN, D. J. See Schoch, R. P.
- BROWN, F. E. See Harkins, W. D.
- BROWNE, A. W. AND OVERMAN, O. R. Oxidation of hydrazine (VII) alleged role of  $\text{HNO}_3$  in formation of  $\text{HN}_2$  ..... 285
- BRUCKMILLER, F. W. Chlorides in presence of thiocyanates ..... 1953
- BRUNEL, R. F. See Wilcox, M.
- BURTON, L. V. See MacArthur, C. G.
- BYERS, H. G. AND LANGDON, S. C. Anodic relations of passive  $\text{Fe}$ —polarization potentials as influenced by external gas pressures ..... 362
- CALVERT, R. P. See Smith, A.
- CARLETON, P. W. Influence of some solvents on rate of action of  $\text{Na}$  with isoamyl bromide. 1128
- CARLSON, A. J., HEKTOEN, L. AND LECOUNT, E. R. Effects of commercial glucose when fed to white rats ..... 930
- CHAPIN, H. C. See Baxter, G. P.
- CHAPIN, R. M. Decomp. of tetrathionates in alk. soln. as source of error in certain I titrations. 625
- CHATTAWAY, F. D. Crystn. of  $\text{Ca}$  tartrate ..... 2519
- CHATTERJEE, N. R. See Datta, R. L.
- CHOUDHURY, J. K. See Datta, R. L.
- CLAPP, F. C. Non-spattering wash bottle ..... 1502
- CLARKE, F. W., THORPE, T. E. AND URBAIN, G. Annual report of International Committee on Atomic Weights, 1917 ..... 2219
- CLEMENS, E. A. See Frank, J. O.
- COLEMAN, A. B. See Bingham, E. C.
- COLEMAN, C. See Schlesinger, H. I.
- CONANT, J. B. See Kelley, G. L.
- COOK, A. N. See Jones, H. I.
- COPE, W. C. AND BARAB, J. Application of nitrometer for detn. of constitution and estn. of  $\text{N}$  in class of nitro-compds. (nitroamines) ..... 2552
- CRAWFORD, F. M. See Schoch, E. P.
- CROMBIE, J. N. See Neidle, M.
- CURTMAN, L. J. AND DASCHAVSKY, P. Silver arsenate test for  $\text{As}$  ..... 1280
- CURTMAN, L. J. AND HARRIS, B. R. Systematic detection of thiocyanates ..... 2622
- DAINS, F. B., O'BRIEN, H. R. AND JOHNSON, C. L. Reactions of formamidines (V) some pyrazolone derivs. .... 1510
- DAINS, F. B., ROBERTS, R. C. AND BREWSTER, R. Q. Action of certain acid reagents on the substituted ureas and thiazole ..... 131
- DAINS, F. B. AND STEPHENSON, A. E. Reactions of the formamidines (VI) some thiazole derivs. 1841
- DALE, J. K. Prepn. of bromoacetylglucose and certain other bromoacetyl sugars, 2187; see Hudson, C. S.
- DALES, B. Elementary Qual. Analysis (book rev.) ..... 2814
- DANCASTER, E. A. See Martin, G.
- DANIELS, E. A. See Hunter, W. H.
- DANIELS, F. Adiabatic calorimeter ..... 1473
- DARRAH, J. E. AND MACARTHUR, C. G. Nitrogenous constituents of brain lecithin ..... 922



- DASCHAVSKY, P. See Curtman, J. J.
- DATTA, R. L. AND CHATTERJEE, N. R. Halogenation (XII) formation of chloropicrin and tetrachloroquinone by action of aqua regia on org. substances, 1813; (XIV) bromination of hydrocarbons by means of Br and  $\text{HNO}_3$ ..... 2545
- DATTA, R. L. AND CHOUDHURY, J. K. Halogenation (X) chloric acid as reagent in org. chemistry, 1079; (XIII) methods of estn. of semicarbazide semioxamamide and oxalylhydrazide by their interactions with halogens and halogen oxyacids..... 2736
- DATTA, A. K. AND DHAR, N. Accuracy of Cu voltameters, 1156; constitution of chromic acid. 1303
- DATTA, R. L. AND FERNANDES, F. V. Halogenation (XI) chlorination with aqua regia—chlorination of hydrocarbons..... 1809
- DAVIS, C. E. See Morgan, J. L. R.
- DAVIS, H. S. Supersatd. solns. of liquids in liquids..... 1166
- DAVISSON, B. S. Titrametric detn. of nitrites..... 1683
- DAY, J. E. See Evans, W. L.
- DEHN, W. M. Baly's theory of chem. reaction and reactivity..... 1
- DERBY, I. H. AND YNGVE, V. Dissociation tensions of certain hydrated chlorides and vapor pressures of their saturated solns..... 1439
- DERICK, C. G. AND BISSELL, D. W. Trimethylene oxide (I) prepn. and characterization. . . 2478
- DERICK, C. G. AND KAMM, O. Structure of dihydro- $\beta$ -naphthoic acids..... 400
- DHAR, N. See Datta, A. K.
- DIGGS, S. H. See Edgar, G.
- DODGE, C. F. See Norris, J. F.
- DODGE, F. D. Some derivs. of coumarin..... 446
- DOELTER, *et al.* Handbuch der Mineralchemie (book rev.)..... 732
- DONNELLY, J. L. See Fry, H. S.
- DOVER, M. V. See Marden, J. W.
- DOX, A. W. AND LAMB, A. R. Accurate aeration method for detn. of alcohol in fermentation mixts. 2561
- DOX, A. W. AND PLAISANCE, G. P. Comparison of barbituric acid, thiobarbituric acid and malonylguanidine as quant. precipitants for furfural, 2156; condensation of thiobarbituric acid with aromatic aldehydes..... 2164
- DROGIN, I. AND ROSANOFF, M. A. Detection and detn. of halogens in org. compds. . . 711
- EASTLACK, H. E. See Smith, A.
- ECKSTEIN, H. C. See Grindley, H. S.
- EDGAR, G. Rapid method for estn. of Cu and Fe, 884; estn. of vanadic acid, after reduction by metallic Ag, 1297; reduction of vanadic acid by HI..... 2369
- EDGAR, G. AND DIGGS, S. H. Diffusion of I in KI solns..... 253
- EDSON, R. See McIntosh, D.
- EDWARDS, V. C. See Wheeler, A. S.
- EGLOFF, G. See Morgan, J. L. R.
- ELLIS, J. H. Free energy of HCl in aqueous soln..... 737
- EMERY, W. O. AND PALKIN, S. Org. periodides (II) periodides of antipyrine, iodiantipyrine and pyrimidine..... 2166
- ESSEX, H., HIBBERT, H. AND BROOKS, B. T. Hydrolysis of chlorpentanes as affected by high pressure: synthetic fusel oil..... 1368
- EVANS, W. L. AND DAY, J. E. Oxidation of EtOH by means of  $\text{KMnO}_4$ ..... 375
- FALK, K. G. AND SUGIURA, K. Comparative study of aeration and heat distn. in Kjeldahl method for detn. of N, 916; studies on enzyme action—corrections..... 921
- FELSING, W. A. See Schoch, E. P.
- FENGER, F. See Long, J. H.
- FERNANDES, V. F. See Datta, R. L.
- FOOTE, H. W. AND SAXTON, B. Effect of freezing on certain inorg. hydrogels ..... 588
- FOSTER, W. Action of  $\text{H}_2\text{S}$  on  $\text{H}_3\text{AsO}_4$ ..... 52
- FRANK, J. O. AND CLEMENS, E. A. Manual of Quant. Chem. Analysis (book rev.) ..... 941
- FRAZER, J. C. W. See Lovelace, B. F.
- FRAZER, J. C. W. AND MYRICK, R. T. Osmotic pressure of sucrose solns. at  $30^\circ$ ..... 1907
- FRIEDEMANN, T. E. See Huston, R. C.
- FRIEND, J. N. Text-book of Inorg. Chemistry (book rev.)..... 730
- FRY, H. S. Further evidence for electronic formula of benzene and the substitution rule, 1323; action of Na methylate on products of nitration of *o*-, *p*- and *m*-chlorotoluenes, 1327; further evidence for electronic tautomerism of benzene derivs..... 1333
- FRY, H. S. AND DONNELLY, J. L. Reactions in non-aqueous solvents (I) action of chromyl chloride upon P trihalides..... 1923
- FURMAN, N. H. See McCay, LeR. W.

- G**ANGLOFF, W. C. See Henderson, W. E.
- GETMAN, F. H. Study of the lead electrode, 792; action of Mg on solns. of KCl..... 2594
- GOMBERG, M. AND VAN STONE, N. E. Triphenylmethyl (XXVI) tautomerism of triarylcarbinols. 1577
- GOMEZ, F. J. S. AND MACHADO, A. R. Elementos de Física Geral (book rev.)..... 939
- GOOCH, F. A. Representative Procedures in Quant. Chem. Analysis (book rev.)..... 940
- GRAHAM, H. T. See Stieglitz, J.
- GRANT, A. J. See James, C.
- GRAY, F. W. Practical Physical Chemistry (book rev.)..... 1905
- GRIFFIN, E. G. See Nelson, J. M.
- GRIFFIN, E. G. AND NELSON, J. M. Influence of certain substances on activity of invertase.... 722
- GRINDLEY, H. S. AND ECKSTEIN, H. C. Nonprotein nitrogenous constituents of feedingstuffs.. 1425
- GROSE, M. R. See Baxter, G. P.
- H**ADLEY, S. E. See Johnson, T. B.
- HAHN, D. A. Reactions of some carboxyl derivs. of trimethylene..... 1517
- HALE, W. J. Studies in cyclopentadiene series (IV) formation of cyclopentadienodihydropyridazines..... 2535
- HALL, R. E. See Harkins, W. D.
- HALL, R. E. AND HARKINS, W. D. Free energy of dilution and f. p. lowerings in solns. of some salts of various types of ionization, and of salt mixts..... 2658
- HALL, W. T. See Treadwell, F. P.
- HALE, W. J. AND HOYT, W. V. Constitution of the 3 symmetrical dinitropyrocolls..... 1065
- HARKINS, W. D. See Hall, R. E.
- HARKINS, W. D. AND BROWN, F. E. App. for accurate and easy detn. of surface tension, with metal thermoregulator for quick adjustment of temp..... 246
- HARKINS, W. D. AND HALL, R. E. At. structure (V) periodic system and properties of elements..... 169
- HARKINS, W. D., HALL, R. E. AND ROBERTS, W. A. Studies on cobaltammines (I) various ionization types as detd. by f. p. lowering in aq. soln., together with conductance measurements..... 2643
- HARKINS, W. D. AND HUMPHERY, E. C. Drop wt. method for detn. of surface tension, 228; app. for detn. of surface tension at interface between two liquids, 236; surface tension at interface between two liquids and effect of acids, salts and bases on interfacial tension.... 242
- HARKINS, W. D. AND PAINE, H. M. Effect of salts on solubility of other salts (VIIIa) solubility relations of very sol. bi-univalent salt..... 2709
- HARKINS, W. D. AND PEARCE, W. T. Ionization and solubility relations of salts of higher types (IV) intermediate ions in solns. of uni-bivalent salts, and of lanthanum iodate, 2679; effect of salts on solubility of other salts (VIIIb) solubility relations of some extremely sol. salts. 2714
- HARKINS, W. D. AND ROBERTS, W. A. Freezing-point lowerings in aq. solns. of salts and mixts. of salts and of salt with nonelectrolyte..... 2676
- HARNED, H. S. H and Cl ion activities of solns. of KCl in 0.1 molal HCl..... 1986
- HARRIS, B. R. See Curtman, L. J.
- HARRIS, G. W. See Richards, T. W.
- HART, M. C. See Heyl, F. W.
- HART, M. C. AND HEYL, F. W. Some constituents of jambul..... 2805
- HARTMAN, M. L. See Baxter, G. P.
- HAW, A. B. See Kober, P. A.
- HAWKINS, C. F. See Baxter, G. P.
- HEKTOEN, L. See Carlson, A. J.
- HEMINGWAY, E. H. See Johnson, T. B.
- HENDERSON, W. E. AND GANGLOFF, W. C. Action of anhydrous  $AlCl_3$  upon unsatd. compds. 1382
- HENRY, W. H. AND MORRISON, F. B. Feeds and Feeding (book rev.)..... 942
- HESSLER, J. C. Alkylcyanoacetic acids..... 909
- HEYL, F. W. See Hart, M. C.
- HEYL, F. W. AND HART, M. C. Constituents of sumbul root..... 432
- HEYROTHE, F. F. Theory of multiple ionization—modification of electrolytic dissociation theory (I) introductory and qual. statement of the theory, with applications..... 57
- HIBBERT, H. See Essex, H.
- HILDEBRAND, J. H. Solubility..... 1452
- HILDEBRAND, J. H. AND BOWERS, W. G. Study of action of alkali on certain Zn salts by means of H electrode..... 785
- HILL, A. J. See Johnson, T. B.
- HILL, J. B. New derivs. of W..... 2383
- HOCKER, C. D. See Bartell, F. E.
- HOLLER, H. D. AND PEPPER, E. L. Density of aqueous solns. of  $CuSO_4$  and  $H_2SO_4$ ..... 1021

- HOLMES, A. See Jacobson, C. A.
- HOLMES, H. N. Inexpensive dialyzer for class use..... 1204
- HOLMES, H. N. AND RINDFUSZ, R. E. Colloidal arsenates and phosphates of Fe..... 1970
- HOLMES, J. E. L. AND JONES, H. C. Action of salts with water of hydration and without water of hydration on velocity of sapon. of esters..... 105
- HOMBERGER, A. W. AND MUNCH, J. C. Quantitative detn. of morphine in various organs when injected into cats and rabbits..... 1873
- HOPKINS, B. S. AND BALKER, C. W. Purification and at. wt. of Yt..... 2332
- HOSTETTER, J. C. See Sosman, R. B.
- HOSTETTER, J. C. AND SOSMAN, R. B. Dissociation of  $\text{Fe}_2\text{O}_3$  in air..... 1188
- HOYT, W. V. See Hale, W. J.
- HUDSON, C. S. Numerical relations among rotatory powers of compound sugars..... 1566, 1904
- HUDSON, C. S. AND BRAUNS, D. H. Cryst.  $\beta$ -methyl fructoside and its tetracetate..... 1216
- HUDSON, C. S. AND DALE, J. K. Isomeric pentacetates of glucosamine and of chondrosamine..... 1431, 2216
- HUDSON, C. S. AND JOHNSON, J. M. Fourth cryst. pentacetate of galactose and some related compds..... 1223
- HUDSON, C. S. AND SAYRE, R. Optical rotatory powers of some acetylated derivs. of maltose, cellose and lactose..... 1867
- HUDSON, C. S. AND YANOVSKY, E. Isomeric alpha and beta hexacetates of  $\alpha$ -glucoheptose.... 1575
- HULFETT, G. A. See Lipscomb, G. F.
- HULL, M. See Long, J. H.
- HUMPHREY, E. C. See Harkins, W. D.
- HUMPHREY, I. W. See Brooks, B. T.
- HUNTER, W. H., OLSON, A. O. AND DANIELS, E. A. Catalytic decompn. of certain phenol Ag salts (I)..... 1761
- HUSTON, R. C. AND FRIEDEMANN, T. E. Action of aromatic alcohols on aromatic compds. in presence of  $\text{AlCl}_3$ ..... 2527
- IBBOTSON, F. AND AITCHISON, L. Analysis of Non-Ferrous Alloys (book rev.)..... 488
- ITO, H. Quantitative detn. of hippuric acid in urine, blood, muscles and liver: method..... 2188
- JACOBSON, C. A. AND HOLMES, A. Alfalfa investigation (VI) alfalfa seed oil..... 480
- JACKSON, C. L. AND BRIGGS, S. A. Derivs. of tetrabromo-*o*-quinone, 676; tetrabromo-*o* phenylenediacetamide..... 685
- JAMES, C. See Bissell, D. W.; Willand, P. S.
- JAMES, C. AND GRANT, A. J. Sepn. of rare earths giving the more sol. double sulfates from Brazilian monazite sand..... 41
- JAMES, C. AND PERLEY, G. A. Extn. of Be from gadolinite..... 875
- JAMES, C. AND WILLAND, P. S. Rare earth cobalticyanides..... 1497
- JOHNSON, C. L. See Dains, F. B.
- JOHNSON, J. M. See Hudson, C. S.
- JOHNSON, L. C. See Noyes, W. A.
- JOHNSON, M. O. Detn. of small quantities of HCN..... 1230, 1645
- JOHNSON, T. B. AND BAILLY, G. C. Amines (V) structure of vitiatine—synthesis of methyl-ethylendiamine..... 2135
- JOHNSON, T. B. AND BATES, J. S. Hydantoins (XXXVIII) synthesis of phenylalanyl-glycine-hydantoin..... 1087
- JOHNSON, T. B. AND HADLEY, S. E. Pyrimidines (LXXXI) secondary-pyrimidine-nucleosides and their unique behavior on hydrolysis..... 1844
- JOHNSON, T. B. AND HEMINGWAY, E. H. Thiocyanates and isothiocyanates (IX) ethyl isothiocyanacetate, 1550; (X) utilization of tetrachloromethylmercaptan for prepn. of alkyl isothiocyanates..... 1860
- JOHNSON, T. B. AND HILL, A. J. Nitrated proteins (V) hydrolysis of nitro-fibroin with  $\text{HCl}$ .... 1392
- JOHNSON, T. B. AND JOYCE, A. W. Pyrimidines (LXXVIII)—reduction of 2-mercapto-6-chloropyrimidines, 1385; (LXXX) mechanism of action of Br on 2-mercaptopyrimidines, 1557; (LXXXII) synthesis of 1,3-diamines by reduction of 2-mercapto-6-oxypyrimidines..... 1854
- JOHNSTON, J. Detn. of carbonic acid, combined and free, in soln., particularly in natural waters..... 947
- JOHNSTON, J. AND WILLIAMSON, E. C. Complete solubility curve of  $\text{CaCO}_3$ ..... 975
- JOHNSTONE, S. J. Rare Earth Industry (book rev.)..... 734
- JONES, DEW. O. See Walton, J. H.
- JONES, H. C. Sapon. of esters, 888; Elements of Physical Chemistry (book rev.), 1144; see Holmes, J. E. L.; Lloyd, H. H.
- JONES, H. I. AND COOK, A. N. Mononitrophenyl ethers..... 1534
- JOYCE, A. W. See Johnson, T. B.

- KAMM, O. See Derick, C. G.
- KAMM, O. AND McCLUGAGE, H. B. Structure of dihydro- $\alpha$ -naphthoic acids. . . . . 419
- KANITZ, A. Temperatur und Lebensvorgänge (book rev.) . . . . . 167
- KARR, W. G. AND LEWIS, H. B. Comparative study of distribution of urea in blood and tissues of certain vertebrates with especial reference to the hen. . . . . 1615
- KARSLAKE, W. J. AND BOND, P. A. 4-Nitro-5-methyl-2-sulfobenzoic acid and some of its derivs. 1338
- KELLEY, G. L. AND CONANT, J. B. Electrometric titration of V. . . . . 341
- KENDALL, J. Addition compds. of phenols with org. acids, 1309; specific cond. of pure  $H_2O$  in equil. with atmospheric  $CO_2$ , 1480; review: prepn. of conductivity  $H_2O$ . . . . . 2460
- KENDALL, J. AND BOOGE, J. E. Studies on catalysis (I) addition compds. of esters with organic acids. . . . . 1712
- KENNEDY, J. J. See Orndorff, W. R.
- KEYES, F. G. AND WINNINGHOFF, W. J. Conductance of solns. of certain iodides in isoamyl and propyl alcohols. . . . . 1178
- KIMBALL, J. W. AND RHID, E. E. Esterification (VIII) esterification of benzoic acid by isomeric butyl mercaptans. . . . . 2757
- KNOWLES, H. I. See Norton, J. F.
- KOBER, P. A. Efficiency of aeration method for detg.  $NH_3$ ; in answer to certain criticisms. . . . 2568
- KOBER, P. A. AND HAW, A. B. Spectrophotometric study of Cu complexes and biuret reactions. . . 457
- KOHLER, E. P. Addition of aliphatic nitro compds. to unsatd. compds. . . . . 889
- KOHLER, E. P. AND PATCH, R. II. Some reactions resulting in cleavage of polynuclear aromatic compds. . . . . 1205
- KRAEMER, H. Scientific and Applied Pharmacognosy (book rev.) . . . . . 162
- KRAUSKOPF, F. C. AND RITTER, G. Colors produced by resorcinol in solns. of certain salts and use of these colors as means of detecting resorcinol in presence of other phenols. . . . . 2182
- KUZIRIAN, S. B. Estn. of Ca in ash of forage plants and animal carcasses. . . . . 1996
- LAMB, A. R. See Dox, A. W.
- LANGDON, S. C. See Byers, H. G.
- LANGMUIR, I. Dissociation of H into atoms (III) mechanism of the reaction, 1145; constitution and fundamental properties of solids and liquids. . . . . 2221
- LECOUNT, E. R. See Carlson, A. J.
- LENHIER, V. Oxidation of Mn solns. in presence of air. . . . . 638
- LENHIER, V. AND MELOCHE, C. C. Vol. detn. of Ce by means of  $KMnO_4$ . . . . . 66
- LENHIER, V. AND TRUOG, E. Quant. detn. of silica. . . . . 1050
- LEVY, S. I. Rare Earths, Their Occurrence, Chemistry and Technology (book rev.) . . . . . 733
- LEWIS, G. N. AND RANDALL, M. Free energy of Br compds. . . . . 2348
- LEWIS, H. A. See Walton, J. H.
- LEWIS, G. N. The atom and the mol. . . . . 762
- LEWIS, H. B. See Karr, W. G.
- LEWIS, W. C. McC. System of Physical Chemistry (book rev.) . . . . . 2217
- LINHART, G. A. Equilibria of  $HgCl_2$  with other chlorides, 1272; potential of Hg electrode against mercurous ion. . . . . 2356
- LIPSCOMB, C. F. AND HULETT, G. A. Calomel standard cell. . . . . 20, 889
- LLOYD, H. H., WIESSEL, J. B. AND JONES, H. C. Conduction of org. acids in abs. EtOH. . . . 121
- LÖHNIS, F. Boden-Bakterien und Boden-Fruchtbarkeit (book rev.) . . . . . 945
- LONG, J. H. Possible Source of error in colorimeter observations, 716; simple cell for detn. of H ion concn. . . . . 936
- LONG, J. H. AND FENGER, F. Reaction of the pancreas and other organs (II) . . . . . 1115
- LONG, J. H. AND HULL, M. Assumed destruction of trypsin by pepsin and acid. . . . . 1620
- LOOMIS, N. E. AND ACREE, S. F. Effect of pressure on potential of H electrode. . . . . 2391
- LOOMIS, N. E. AND MEACHAM, M. R. Study of 0.1 N HCl-calomel electrode. . . . . 2310
- LOTHROP, A. P. Lab. Course in Org. and Physiological Chemistry (book rev.) . . . . . 1905
- LOVELACE, B. F., FRAZER, J. C. W. AND MILLER, E. V. p. of solns.—lowering of v. p. of water produced by dissolved KCl. . . . . 515
- LUBS, H. A. AND ACREE, S. F. The sulfonphthalein series on indicators and the quinone-phenolate theory. . . . . 2772
- MACARTHUR, C. G. See Darrah, J. E.
- MACARTHUR, C. G. AND BURTON, L. V. Brain cephalin (II) fatty acids. . . . . 1375
- MCCAY, LER. W. AND FURMAN, N. H. Use of HF in sepn. of heavy metals from Sn, Sb, W and Mo by means of elec. current. . . . . 640
- McCLUGAGE, H. B. See Kamm, O.
- MCDONNELL, C. C. AND SMITH, C. M. Arsenates of Pb (I), 2027; (II) equil. in system  $PbO$ ,  $As_2O_3$ ,  $H_2O$ . . . . . 2366

MACDOUGALL, F. H. Equation of state for gases and liquids.....	528
McFARLAND, B. W. Practical Elementary Chemistry (book rev.).....	487
MACHADO, A. R. See Gomez, F. J. S.	
McHARGUE, J. S. Chem. changes occurring during ripening of wild goose plum.....	718
McINTOSH, D. See Reid, H. S.	
McINTOSH, D. AND EDSON, R. Colloidal solid solns.....	613
McLAREN, D. See Qua, N. C.	
McMULLEN, T. C. Me ester of <i>o</i> -benzoylbenzoic acid.....	1278
McNAIR, J. B. Poisonous principle of poison oak.....	1417
McPHERSON, A. T. See Bailey, J. R.	
McPHERSON, W. AND HENDERSON, W. E. Lab. Exercises Arranged to Accompany "First Course in Chemistry" (book rev.).....	168
MAGNANINI, G. AND VENTURI, A. Improvement of Hoffman's eudiometer.....	1203
MARDEN, J. W. Solubilities of sulfates of Ba, Sr, Ca and Pb in $\text{AcONH}_4$ solns. at 25° and criticism of present methods for sepn. of these substances by means of $\text{AcONH}_4$ solns.....	310
MARDEN, J. W. AND DOVER, M. V. Solubilities of several substances in mixed nonaq. solns.	1235
MARTIN, F. H. See Smith, D. P.	
MARTIN, G. AND DANCASTER, E. A. Halogens and their Allies (book rev.).....	730
MARTIN, H. C. <i>o</i> -Benzoylbenzoyl chloride.....	1142
MATHEWS, A. P. Physiological Chemistry (book rev.).....	165
MEACHAM, M. R. See Loomis, N. E.	
MELOCHE, C. C. See Lenher, V.	
MENDL, L. B. Changes in Food Supply and Their Relation to Nutrition (book rev.).....	1437
MERWIN, H. E. See Raukin, G. A.	
MICHAEL, A., SCHARF, E. AND VOIGT, K. Rearrangement of iso into tertiary butyl bromide....	653
MIDDLETON, A. R. AND MILLER, H. L. Detection of Ni in Co salts.....	1705
MIKESKA, L. A. See Bailey, J. R.	
MILLER, E. See Lovelace, B. F.	
MILLER, H. L. See Middleton, A. R.	
MORGAN, A. F. Mol. rearrangement of some triarylmethylchloroamines.....	2095
MORGAN, J. L. R. AND EGGLOFF, G. Properties of mixed liquids (II) $\text{PhOH-H}_2\text{O}$ and $\text{NEt}_3\text{-H}_2\text{O}$ mixts.....	844
MORGAN, J. L. R. AND DAVIS, C. E. Properties of mixed liquids (I) $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ mixts.....	555
MORGAN, R. See Livingston, J.	
MORRISON, F. B. See Henry, W. H.	
MOSHS, D. V. See Plaisance, G. P.	
MUNCH, J. C. See Homberger, A. W.	
MUNCIE, F. W. See Beal, G. D.	
MURPHY, J. S. See Norris, J. F.	
MYRICK, R. T. See Frazer, J. C. W.	
NEAL, O. D. Bottle for iodometric titration of Cu.....	1308
NEIDLE, M. Temp. effect in dialysis and simple rapid dialyzer.....	1270
NEIDLE, M. AND BARAB, J. Dialysis. (I) Dialysis of a colloidal soln. of hydrous chromic oxide in $\text{CrCl}_3$ .....	1961
NEIDLE, M. AND CROMBIE, J. N. Oxidation-reduction reactions without the addition of acid (III) $\text{FeCl}_3$ and $\text{KMnO}_4$ .....	2607
NEIDLE, M. AND WITT, J. C. Oxidation and reduction without addition of acid (II) reaction between $\text{SnCl}_2$ and $\text{K}_2\text{Cr}_2\text{O}_7$ —contribution to colloid chemistry.....	47
NELSON, B. E. Compn. of neurokeratin.....	2558
NELSON, J. M. See Griffin, E. G.; Northrop, J. H.	
NELSON, J. M. AND GRIFFIN, E. G. Adsorption of invertase.....	1109
NEUN, D. E. See Sherman, H. C.	
NEWELL, L. C. Lab. Manual of Inorg. Chemistry for Colleges (book rev.).....	2813
NORRIS, J. F., ROONEY, K. E., MURPHY, J. S. AND DODGE, C. F. Org. mol. compds.....	702
NORRIS, J. F., WATT, M. AND THOMAS, R. Reaction between alcs. and aq. solns. of $\text{HCl}$ and $\text{HBr}$ .....	1071
NORTHROP, J. H. AND NELSON, J. M. Phosphoric acid in starch.....	472
NORTON, J. F. See Woodman, A. G.	
NORTON, J. F. AND KNOWLES, H. I. Study of indicators for detn. of temporary hardness in $\text{H}_2\text{O}$ .....	877
NOYES, W. A. AND JOHNSON, L. C. Supposed effect of form of container on density of a gas.	1017
O'BRIEN, H. R. See Dains, F. B.	
OLSON, A. O. See Hunter, W. H.	

- ORNDORFF, W. R. AND KENNEDY, J. J. Nitration products of phenoltetrachlorophthalein and some of their derivs. .... 2486
- ORNDORFF, W. R. AND ROSE, C. C. Diethylamino-*m*-hydroxybenzoyltetrachlorobenzoic acid and trichlorodiethylaminooxantho<sup>n</sup>carboxylic acid and some of their derivs. .... 2101
- OSTWALD, WOLFGANG. Handbook of Colloid Chemistry (book rev.)..... 733
- OVERMAN, O. R. See Browne, A. W.
- PAINE, H. M. See Harkins, W. D.
- PALKIN, S. Sepn. of Li from other alkali metals, 2326; see Emery, W. O.
- PARKER, H. G. Crucible "fork"..... 1203
- PATCH, R. H. See Kohler, E. P.
- PEARCE, W. T. See Harkins, W. D.
- PEFFER, E. L. See Holler, H. D.
- PERLEY, G. A. See James, C.
- PETER, A. M. Stability of Ag-fulminate under water..... 486
- PHILLIPS, F. C. Chem. German (book rev.)..... 161
- PHIPPS, T. E. See Schoch, E. P.
- PLAISANCE, G. P. See Dox, A. W.
- PLAISANCE, G. P. AND MOSES, D. V. Device for regulating pump used in exhausting vacuum oven..... 1063
- PLIMMER, R. H. A. Practical Org. and Biochemistry (book rev.)..... 164
- PRITCHETT, R. H. See Schoch, E. P.
- PUNNETT, P. W. See Sherman, H. C.
- QUA, N. C. AND McLAREN, D. Action of soln. of KOH in alcohol on oxalic esters..... 180
- RAE, W. N. Blackening of yellow P..... 887
- RANDALL, M. Extrapolation of conductance values, 788; see Lewis, G. N.
- RANDALL, M., BICHOWSKY, F. R. v. AND RODEBUSH, W. H. Practical installation of double combination potentiometer..... 1266
- RANKIN, G. A. AND MERWIN, H. E. Ternary system: CaO-Al<sub>2</sub>O<sub>3</sub>-MgO..... 568
- REID, E. E. See Kimball, J. W.; Sachs, J. H.; Van Epps, G. D.; Wroth, B. B.
- REID, H. S. AND MCINTOSH, D. Cryoscopic measurements at low temps..... 615
- RICHARDS, T. W. Suggestion concerning statement of phase rule, 983; free energy and heat capacity—reply to paper by James M. Bell..... 2631
- RICHARDS, T. W. AND ANDEREGG, F. O. Inclusions in Ag voltameter..... 2044
- RICHARDS, T. W. AND HARRIS, G. W. Floating equil..... 1000
- RICHARDS, T. W. AND SHIPLEY, J. W. Compressibility of certain typical hydrocarbons, alcs. and ketones..... 989
- RICHARDS, T. W. AND WADSWORTH, C., 3D. Density of Pb from radioactive minerals, 221; density of radio-lead from pure Norwegian cleveite, 1658; further study of at. wt. of Pb of radioactive origin..... 2613
- RINDFUSZ, R. E. See Holmes, H. N.
- RITTER, G. See Krauskopf, F. C.
- ROBERTS, R. C. See Dains, F. B.
- ROBERTS, W. A. See Harkins, W. D.
- RODEBUSH, W. H. See Randall, M.
- ROONEY, K. E. See Norris, J. F.
- ROSANOFF, M. A. See Drogin, I.
- ROSE, C. C. See Orndorff, W. R.
- RUSSELL, E. J. Soil Conditions and Plant Growth (book rev.)..... 944
- RUSSELL, G. A. Volatile oil of *Euthamia caroliniana* (L) Green..... 1398
- SACHS, J. H. AND REID, R. E. Esterification (VII) esterification of *o*-, *m*- and *p*-toluic acids by ethyl mercaptan..... 2746
- SAXTON, B. See Foote, H. W.
- SAYRE, R. See Hudson, C. S.
- SCATCHARD, G. See Bogert, M. T.
- SCHARF, E. See Michael, A.
- SCHLESINGER, H. I. See Bingham, E. C.
- SCHLESINGER, H. I. AND COLEMAN, C. Cond. (III) behavior of alkali metal formates in (anhydrous) formic acid..... 271
- SCHOCH, E. P. Chemistry in the High School (book rev.)..... 1437
- SCHOCH, E. P., BROWN, D. J. AND PHIPPS, T. E. Electro-analytical method for detn. and sepn. of metals of Cu-Sn group..... 1660
- SCHOCH, E. P. AND CRAWFORD, F. M. Electroanalysis of Ag with solns. of AgCl in NH<sub>3</sub>..... 1682

- SCHOCH, E. P. AND FELSING, W. A. Influence of K ion and of Ca ion on ferri-ferrocyanide potential..... 1928
- SCHOCH, E. P. AND PRITCHETT, R. H. Electrolytic prepn. of hydroxylamine hydrochloride.... 2042
- SENIOR, J. K. Mol. rearrangement of triarylmethylazides, 2718; see Stieglitz, J.
- SHEPARD, N. A. Amines (VI) utilization of hypochlorite color reactions in establishing mechanism of action of  $\text{MeSO}_3$  on aniline..... 2507
- SHEPARD, N. A. AND TICKNOR, A. A. Amines (V) formation of Schiff bases from  $\beta$ -phenylethylamine and their reduction to alkyl derivs. of this amine..... 381
- SHERMAN, H. C. AND BAKER, J. C. Expts. on starch as substrate for enzyme action..... 1885
- SHERMAN, H. C. AND NEUN, D. E. Exams. of certain methods for study of proteolytic action.. 2199
- SHERMAN, H. C. AND PUNNETT, P. W. Products of action of certain amylases on sol. starch, with special reference to formation of glucose..... 1877
- SHERMAN, H. C. AND TANBERG, A. P. Expts. on amylase of *Aspergillus oryzae*..... 1638
- SHIPLEY, J. W. Sodium pyrogallate as reagent for detn. of O, 1687; see Richards, T. W.
- SILL, H. F. Influence of pressure on solubility..... 2632
- SMITH, A. AND CALVERT, R. P. Dissociation pressures of  $\text{HgCl}_2$ ..... 801
- SMITH, A. AND EASTLACK, H. E. Allotropy and solubilities in  $\text{H}_2\text{O}$  of  $\text{NH}_4\text{Br}$ , 1261;  $\text{NH}_4\text{I}$ , its solubilities and the absence of transition point..... 1500
- SMITH, C. M. See McDonnell, C. C.
- SMITH, D. P. AND MARTIN, F. H. Occlusion of H by Pd cathode..... 2577
- SMITH, G. E. Lead arsenates—study of factors controlling reactions of Pb nitrate and Pb acetate with  $\text{Na}_2\text{HAsO}_4$ ..... 2014
- SOSMAN, R. B. See Hostetter, J. C.
- SOSMAN, R. B. AND HOSTETTER, J. C. Oxides of Fe (I) solid soln. in system  $\text{Fe}_2\text{O}_3$ - $\text{Fe}_3\text{O}_4$ .... 807
- SPIEGEL, L. Chem. Constitution and Physiological Action (book rev.)..... 165
- STAGNER, B. A. Mol. rearrangement of triarylmethylhydroxylamines, 2069; see Stieglitz, J.
- STARK, J. Elektrische Spectroanalyse Chemischer Atome (book rev.)..... 732
- STARKWEATHER, H. W. See Baxter, G. P.
- STEARNS, A. E. See Young, S. W.
- STEPHENSON, A. E. See Dains, F. B.
- STEWART, O. J. See Baxter, G. P.
- STIEGLITZ, J. AND GRAHAM, H. T. Thermal decompn. of symmetrical diarylhydrazines.... 1736
- STIEGLITZ, J. AND SENIOR, J. K. Mol. rearrangement of *sym-bis*-triarylmethylhydrazines.... 2727
- STIEGLITZ, J. AND STAGNER, B. A. Mol. rearrangements of  $\beta$ -triphenylmethyl- $\beta$ -methyl hydroxylamines and theory of mol. rearrangements..... 2046
- STRACHAN, E. K. Nonideal solns.—activity of difficultly sol. component..... 626
- SUGIURA, K. See Falk, K. G.
- SWANSON, C. O. AND TAGUE, E. L. Certain conditions which affect activity of proteolytic enzymes in wheat flour..... 1098
- SWENNEY, O. R. Analysis of certain W derivs..... 2377
- TAGUE, E. L. See Swanson, C. O.
- TANBERG, A. P. See Sherman, H. C.
- TAYLOR, H. S. Interaction of H and Cl under influence of  $\alpha$ -particles, 280; thermodynamic properties of Ag and Pb iodides..... 2295
- TAYLOR, W. A. AND ACREH, S. F. Studies in measurement of elec. cond. of solns. at different frequencies—(V) use of Vreeland oscillator and other sources of current for cond. measurements, 2396; (VI) investigations on bridge methods, resistances, cells, capacities, inductances, phase relations, precision of measurements, and comparison of resistances obtained by use of inductance and capacity bridges, 2403; (VII) investigations on true and apparent resistances, voltage, apparent capacity, size and character of electrodes, ratio of inductance changes to resistance changes, and relation of induction and capacity to frequency..... 2415
- THOMAS, R. See Norris, J. F.
- THORPE, SIR E. Alcoholometric Tables (book rev.)..... 163
- THORPE, T. E. See Clarke, F. W.
- TICKNOR, A. A. See Shepard, N. A.
- TOWER, O. F. Viscosity of certain alcoholic solns..... 833
- TREADWELL, F. P. AND HALL, W. T. Qual. Analysis (book rev.)..... 1645
- TRUOG, E. See Lehner, V.
- TURNER, B. B. Chem. compn. of *Oscillatoria prolifica*..... 1402
- TUTTLE, J. R. See Bogert, M. T.
- UCHIDA, S. Essential oil of sugi leaves, 687; essential oil of Formosan Hinoki wood..... 699
- UNDERHILL, F. P. Physiology of the Amino Acids (book rev.)..... 943
- URBAIN, G. See Clarke, F. W.

- VAN EPPS, G. D. AND REID, E. E. Prepn. of nitriles (II) aliphatic nitriles, 2120; (III) catalytic prepn. .... 2128
- VAN STONE, N. E. See Gomberg, M.
- VAN ZOEREN, G. J. Convenient dip electrode. .... 652
- VENTURI, A. See Magnanini, G.
- VINAL, G. W. AND BOVARD, W. M. Inclusions in Ag voltameter deposits. .... 496
- VOIGT, K. See Michael, A.
- VOSBURGH, I. Mol. rearrangement of triphenylmethylhalogenamines. .... 2081
- WADSWORTH, C., 3d. See Richards, T. W.
- WALLACE, C. C. See Baxter, G. P.
- WALTON, J. H. AND BRANN, A. Effect of dissolved substances on velocity of crystn. of water (I), 317; (II) existence of hydrates in soln. as explanation of retarding effect of solute on velocity of crystn. of  $H_2O$ . .... 1161
- WALTON, J. H. AND JONES, DEW. O. Catalytic decompn. of  $H_2O_2$  in certain non-aqueous solns. 1956
- WALTON, J. H. AND LEWIS, H. A. Partition coeffs. of  $H_2O_2$  between water and org. solvents. 633
- WASHBURN, E. W. Introduction to Principles of Physical Chemistry, from Standpoint of Modern Atomistics and Thermodynamics (book rev.), 944; measurement of electrolytic cond. (I) theory of design of cond. cells. .... 2431
- WATT, M. See Norris, J. F.
- WEAVER, E. R. Colorimetric detn. of  $C_2H_2$ . .... 352, 653
- WEBER, H. C. P. See Welch, J. M.
- WEBER, H. C. P. AND WINKELMANN, H. A. Systematic sepn. of anions of group I—anions whose Ag salts are insol. in  $HNO_3$ . .... 2000
- WEEKS, L. F. See Adams, R.
- WELCH, J. M. AND WEBER, H. C. P. Sepn. of metals of tin group. .... 1011
- WHEELER, A. S. AND EDWARDS, V. C. New case of tautomerism: 1,4,5,6-tetrahydroxynaphthalene. .... 387, 1144
- WHITCOMB, W. H. See Baxter, G. P.
- WIESEL, J. B. See Lloyd, H. II.
- WILLAMAN, J. J. Modification of Pratt method for detn. of citric acid. .... 2193
- WILLAND, P. S. See James, C.
- WILLAND, P. S. AND JAMES, C. Sepn. of erbium from yttrium. .... 1198
- WILLCOX, M. AND BRUNEL, R. F. Reversible replacement of alcs. in aldehydealcoholates, 1821; mol. wt. of some alcoholates of chloral and butylchloral in benzene soln. .... 2533
- WILLIAMSON, E. D. See Johnston, J.
- WILSON, J. A. Theory of colloids. .... 1982
- WINKELMANN, H. A. See Weber, H. C. P.
- WINNINGHOFF, W. J. See Keyes, F. G.
- WITT, J. C. See Neidle, M.
- WITZEMANN, E. J. Role of atm. O in oxidation of glucose with  $KMnO_4$  in presence of varying amts. of alkali—products of oxidation. .... 150
- WOODMAN, A. G. Food Analysis, Typical Methods and Interpretation of Results (book rev.). 941
- WOODMAN, A. G. AND NORTON, J. F. Air, Water and Food from Sanitary Standpoint (book rev.). 735
- WOOLLEY, G. H. Silver salt of triiodophenol and its catalytic decompns. .... 2474
- WRIGHT, F. E. Petrographic microscope in analysis. .... 1647
- WROTH, B. B. AND REID, E. E. Solubilities of liquids in liquids—partition of lower alcohols between  $H_2O$  and cottonseed oil. .... 2316
- WYCKOFF, R. W. G. App. for detg. ions in soln. .... 1711
- YANOVSKY, E. See Hudson, C. S.
- YNGVE, V. See Derby, I. H.
- YOUNG, S. W. AND STEARN, A. E. Basic copper sulfates. .... 1947



# Subject Index to Volume XXXVIII, 1916.

<b>ACETANILIDE</b> soly. in $\text{Et}_2\text{O-CHCl}_3$ solns., 1242; soly. in acetone-benzene solns. ....	1244
Acetanisidine hydriodide. ....	145
Acetanisidine hydriodo-diiodide. ....	148
Acetochlorogalactose. ....	1226
Acetone detn. of, in systems of $\text{MeOH}$ , $\text{H}_2\text{O}$ and $\text{KF}$ and equil. in systems of $\text{Me Et}$ ketone, $\text{H}_2\text{O}$ and inorg. salts. ....	1136
Acetophenone, action of aqua regia on. ....	1820
Acetphenetidine hydriodide. ....	145
Acetphenetidine hydriodo-diiodide. ....	145
Acetphenetidine hydriodo-tetraiodide. ....	146
3-Acetyl-4-benzalhydantoin. ....	1092
Acetylene, colorimetric detn. of, 352, 653; action upon anhydrous and upon alc. solns. of $\text{AlCl}_3$ . .	1383
Acidimetry, indicator for. ....	1606
Acids, conductivities of certain org., in abs. $\text{EtOH}$ , 121; catalyses with weak, 901; addition compds. of phenols with org., 1309; relations between constants of dibasic, and of amphoteric electrolytes, 1503; catalysis (I) addition compds. of esters with org., 1712; reaction of both ions and nonionized forms of, bases and salts. ....	2145
Acönitic acid, cond. in abs. $\text{EtOH}$ . ....	126
Acrylic acid, $\text{NH}_4$ salt of. ....	1796
Adsorption of invertase, 1109; of gases by solids, 2267; exptl. evidence, that is chem. phenomena, 2269; phenomena at higher gas pressures, 2282; hy porous bodies. ....	2285
Air from Sanitary Standpoint (Woodman, Norton, book review) ....	735
Alcoholimetry, Alcoholometric Tables (Thorpe, book review). ....	163
Alcohols, zingiberol, 430; compressibility of certain typical, 989; reaction between, and aq. solns. of $\text{HCl}$ and $\text{HBr}$ , 1071; reversible replacement of, in aldehydealcoholates, 1821; partition of lower, between $\text{H}_2\text{O}$ and cottonseed oil, 2316; action of oxalyl chloride on primary, secondary and tertiary, 2514; action of aromatic, on aromatic compds. in presence of $\text{AlCl}_3$ . ....	2527
Aldehydealcoholates, reversible replacement of alcs. in. ....	1821
Aldehydes, condensation of thiobarbituric acid with aromatic. ....	2416
Alfalfa seed oil. ....	480
Alkalies action on certain $\text{Zn}$ salts. ....	785
Alkali metal formates, behavior in (anhydrous) formic acid. ....	271
Alkali metal halides, changes in vol. on soln. in water of (II), 70; densities and cubical coeffs. of expansion of. ....	259
Alkali metals, sepn. of $\text{Li}$ from other. ....	2326
Alkalimetry, indicator for. ....	1606
Alkylcyanoacetic acids. ....	909
Alkyl isothiocyanates, utilization of tetrachloromethylmercaptan for the prepn. of. ....	1860
Allotropy of $\text{NH}_4\text{Br}$ . ....	1261
Alloys, Analysis of Non-Ferrous (Ibbotson, Aitchison, book review). ....	488
Allylmalonic acid, cond. in abs. $\text{EtOH}$ . ....	125
Allylmalonic acid, $\text{NH}_4$ salt of. ....	1799
Allyl mustard oil, action of aqua regia on. ....	1817
Alpha particles, interaction of $\text{H}$ and $\text{Cl}$ under influence of. ....	280
Aluminium detn. as oxide. ....	1282
Aluminium chloride, action of anhydrous, on unsatd. compds., 1382; action of aromatic alcohols on aromatic compds. in presence of. ....	2527
Aluminium oxide, system: $\text{CaO-Al}_2\text{O}_3\text{-MgO}$ , 568; hydrogels. ....	588
Amides, pyrogenetic decompn. of. ....	2503, 2505
Amidines synthesis from cyanamides. ....	2768
Amines, 381, 2135; utilization of hypochlorite color reactions in establishing mechanism of action of $\text{MeSO}_4$ on aniline. ....	2507
Amino acids, spectrophotometric study of $\text{Cu}$ complex of, 457; Physiology of the (Underhill, book review). ....	943
Aminobenzoic acids, cond. in abs. $\text{EtOH}$ of <i>o</i> - and <i>p</i> -. ....	126, 127
2-Amino-4,6-dibromoacetanilide. ....	686
Aminoethyl alcohol in brain lecithin. ....	922
<i>p</i> -Aminophenol, action of aqua regia on. ....	1817
Ammonia, efficiency of aeration method for distg., 2568; presence in diseased plants—its significance with regard to crop rotation and soil depletion. ....	2572

Ammonium acetate solubilities of sulfates of Ba, Sr, Ca and Pb in, solns. at 25° and criticism of present methods for sepn. of these substances by means of, solns. ....	310
Ammonium bromide, allotropy and solubilities in H <sub>2</sub> O of. ....	1261
Ammonium iodide, its solubilities and the absence of a transition point. ....	1500
Amphoteric electrolytes, relation between constants of dibasic acids and. ....	1503
Amylase of <i>Aspergillus oryzae</i> , 1638; products of action of certain, on sol. starch, with special reference to formation of glucose. ....	1877
Analysis, bath used for soln. of samples in O-free atm., 374; of Non-Ferrous Alloys (Ibbotson, Aitchison, book review), 488; Representative Procedures in Quant. Chem. (Gooch, book review), 940; Manual of Quant. Chem. (Frank, Clemens, book review), 941; Qual. (Treadwell, Hall, book review), 1645; petrographic microscope in, 1647; electro-analytical method for detn. and sepn. of metals of Cu-Sn group, 1660; systematic sepn. of anions of group I— anions whose Ag salts are insol. in nitric acid, 2000; Elementary Qual. (Dales, book review). ....	2814
Aniline, action of aqua regia on, 1818; utilization of hypochlorite color reactions in establishing mechanism of action of MeSO <sub>4</sub> on, 2507; identification of. ....	2725
Aniline black, action of aqua regia on. ....	1819
Aniline chlorate, prepn. of. ....	1080
Anions, systematic sepn. of, of group I— anions whose Ag salts are insol. in HNO <sub>3</sub> . ....	2000
Anisalcohol. ....	1212
Anisic acid cond. in abs. EtOH. ....	127
$\beta$ -Anisoxypropionic acid. ....	1533
Antimony, use of HF in sepn. of heavy metals from, by means of elec. current, 640; sepn. of As, Sn and, 1011; detn. of. ....	1672
Antipyrine periodide. ....	2166
Aqua regia chlorination with, 1809; formation of chloropicrin and tetrachloroquinone by action of, on org. substances. ....	1813
Aromatic compounds, some reactions resulting in cleavage of polynuclear, 1205; action of aromatic alcohols on, in presence of AlCl <sub>3</sub> . ....	2527
Arsenic, sepn. of Sb, Sn and, 1011; silver arsenate test for. ....	1280
Arsenic acid, action of H <sub>2</sub> S on. ....	52
Arsenic pentoxide, equil. in system PbO, As <sub>2</sub> O <sub>5</sub> , H <sub>2</sub> O. ....	2366
Arsenious oxide, density and cubical coeff. of expansion of. ....	266
<i>Aspergillus oryzae</i> , amylase of. ....	1638
Atomic weights, 23rd ann. rept.—detns. published during 1915, 489; ann. rept. of Intern. Comm., 1917, 2219; see also the various elements.	
Atomistics, Introduction to Principles of Physical Chemistry, from Standpoint of Modern, and Thermodynamics (Washburn, book review). ....	944
Atomic structure. ....	169
Atoms, the, and the mol. ....	762
Azobenzene, action of aqua regia on. ....	1819
<b>BACTERIA</b> , Boden-Bakterien und Boden-Fruchtbarkeit (Löbner, book review). ....	945
Baly's theory of chem. reaction and reactivity. ....	1, 15, 227
Barbituric acid, comparison of, thiobarbituric acid and malonylguanidine as quant. precipitants for furfural. ....	2156
Barium sulfates, soly. in AcONH <sub>4</sub> solns. at 25° and criticism of present methods for sepn. of the sulfates of Ba, Sr, Ca and Pb by means of AcONH <sub>4</sub> solns. ....	310
Bases, reaction of both ions and nonionized forms of acids, salts, and. ....	2145
Bath for soln. of ssmpls in an O-free atmosphere. ....	374
Behenic acid in alfalfa seed oil. ....	485
$\beta$ -Benzal- $\beta$ -anisoxydimethylmalonic acid, Me ester of. ....	1526
Benzal- $\beta$ -anisoxypropionic acids. ....	1531
$\alpha$ -Benzal- $\gamma$ -anisylocrotonolactone. ....	1530
4-Benzalhydantoin-1-acetic acid and Et ester. ....	1092, 1093
Benzal- $\beta$ -phenylethylamine. ....	383
Benzamide, action of aqua regia on. ....	1819
Benzene, electronic formula of, and the substitution rule, 1323; mol. wt. of some alcoholates of chloral and butylchloral in, soln. ....	2533
Benzene derivatives, electronic tautomerism of. ....	1333
Benzene series, presence of benzene homologs in high boiling distillates of petroleum. ....	393
Benzenesulfonic acid, action of aqua regia on. ....	1819
Benzhydrol, action of oxalyl chloride on. ....	2518
Benzidine, action of aqua regia on. ....	1819
Benzilic acid, cond. in abs. EtOH. ....	125

Benzoic acid, cond. in abs. EtOH, 126; soly. in Et <sub>2</sub> O-CHCl <sub>3</sub> solns., 1243; soly. in acetone-benzene and in EtOAc-benzene solns., 1244; esterification by isomeric butyl mercaptans.....	2757
Benzophenone, action of aqua regia on, 1820; identification of.....	2724
Benzophenonechloroimide, attempt to effect rearrangement of.....	2094
Benzotriphenylmethylamide.....	2087
o-Benzoylbenzoic acid, Me ester of.....	1228
o-Benzoylbenzoyl chloride.....	1142
o-Benzoylbenzoyl cyanide.....	1143
Benzyl alcohol, action of oxalyl chloride on.....	2517
Benzylamine chlorate.....	1082
4-Benzylhydantoin.....	1094
4-Benzylhydantoin-1-acetic acid, Et ester of.....	1095
Benzylethylamine chlorate.....	1082
4-Benzylhydantoin-1-acetic acid.....	1095
Benzylidenehydrazinoacetic-isobutyric acid, K salt of.....	1780
Benzylidenehydrazinoacetic-propionic acid, Na salt of.....	1780
Benzylidenehydrazinodiacetic acid.....	1778
Benzylidenehydrazinodipropionic acid, K salt of.....	1781
Benzylmalonic acid, cond. in abs. EtOH, 125; NH <sub>4</sub> salt of.....	1799
Benzylmethylaniline chlorate.....	1082
Benzyl-β-phenylethylamine.....	383
Beryllium, extn. from gadolinite.....	875
Beryllium vanadates.....	2361
Binary mixtures, properties of H <sub>2</sub> SO <sub>4</sub> -H <sub>2</sub> O mixts.....	555
Bismuth, detn. of.....	1672
Biuret reaction, spectrophotometric study of Cu complexes and.....	457
Blood, distribution of urea in, of certain vertebrates with especial reference to the hen, 1615; detn. of hippuric acid in.....	2188
<b>BOOKS, NEW: REVIEWS</b> —Chem. German (Phillips), 161; Scientific and Applied Pharmacognosy (Kraemer), 162; Alcoholometric Tables (Thorpe), 163; Practical Org. and Biochemistry (Plimmer), 164; Chem. Constitution and Physiological Action (Spiegel), 165; Physiological Chemistry (Mathews), 165; Temperatur und Lebensvorgänge (Kanitz), 167; Lab. Exercises Arranged to Accompany "First Course in Chemistry" (McPherson, Henderson), 168; Practical Elementary Chemistry (McFarland), 487; Analysis of Non-Ferrous Alloys, 488; Text-Book of Inorg. Chemistry—The Halogens and their Allies (Friend, Martin, Dancaster), 730; Ueber das periodische System der chemischen Elemente (Bilecki), 732; Handbuch der Mineralchemie (Doelter, <i>et al.</i> ), 732; Electricische Spectroanalyse Chemischer Atome (Stark), 732; Handbook of Colloid Chemistry (Ostwald), 733; Rare Earths, Their Occurrence, Chemistry and Technology (Levy), 733; Rare Earth Industry (Johnstone), 734; Air, Water and Food from Sanitary Standpoint (Woodman, Norton), 735; Journal of Assoc. of Official Agricultural Chemistry, 736; Elementos de fisica geral (Gomez, Machado), 939; Quant. Laws in Biological Chemistry (Arrhenius), 939; Representative Procedures in Quant. Chem. Analysis (Gooch), 940; Manual of Quant. Chem. Analysis (Frank, Clemens), 941; Food Analysis, Typical Methods and Interpretation of Results (Woodman), 941; Feeds and Feeding (Henry, Morrison), 942; Physiology of the Amino Acids (Underhill), 943; Soil Conditions and Plant Growth (Russell), 944; Introduction to Principles of Physical Chemistry, from Standpoint of Modern Atomistics and Thermodynamics (Washburn), 944; Boden-Bakterien und Boden-Fruchtbarkeit (Löhnis), 945; Elements of Physical Chemistry (Jones), 1144; Annuaire pour l'an 1916, 1260; Chemistry in High School (Schoch), 1437; Changes in Food Supply and Their Relation to Nutrition (Mendel), 1437; Qual. Analysis (Treadwell, Hall), 1645; Practical Physical Chemistry (Gray), 1905; Lab. Course in Org. and Physiological Chemistry (Lothrop), 1905; System of Physical Chemistry (Lewis), 2217; Annual Reports of Progress of Chemistry for 1915, 2576; Elementary Qualitative Analysis (Dales), 2814; Lab. Manual of Inorg. Chemistry for Colleges (Newell).....	
Bromates detn. of periodates, iodates, chlorates and, in presence of each other.....	330
Brometone acetic ester.....	2740
Bromides, systematic sepn. of anions of group I.....	2000
Bromination of hydrocarbons by means of Br and HNO <sub>3</sub> .....	2545
Bromine, mechanism of action of, on 2-mercaptopyrimidines.....	1557
Bromine compounds, free energy of.....	2348
Bromoacetylglucose, prep. of.....	2187
Bromodinitrophenoltetrachlorophthalein.....	2492
p-Bromohydrazobenzene, velocity of decompn. of.....	1753
3-Bromo-4-methoxybenzylhydrol.....	1215

$\gamma$ -Bromo- $\gamma$ -nitro- $\beta$ -phenyl- $\alpha$ -bromobutyrophenone.....	897
$\gamma$ -Bromo- $\gamma$ -nitro- $\beta$ -phenylbutyrophenone.....	894
$\gamma$ -Bromo- $\gamma$ -nitro- $\beta$ -phenylvalerophenone.....	
Bromopalmitic acid, cond. in abs. EtOH, 124; $\text{NH}_4$ salt of $\alpha$ .....	1794
<i>p</i> -Bromophenyl- <i>p</i> -chlorophenylphenylmethylchloroamine.....	2100
<i>p</i> -Bromophenyldiphenylmethylhydroxylamine.....	2071
<i>p</i> -Bromophenyldiphenylmethylhydroxylamine hydrochloride, rearrangement of.....	2074
<i>p</i> -Bromophenyldiphenylmethyl- $\beta$ -methylhydroxylamines, rearrangement of.....	2067, 2068
Bromopropionic acid, action on hydrazine hydrate, 1782; $\text{NH}_4$ salt of $\alpha$ .....	1790
$\alpha$ -Bromostearic acid, $\text{NH}_4$ salt of.....	1795
Bromosuccinic acid, cond. in abs. EtOH, 125; $\text{NH}_4$ salt of.....	1800
Brain, nitrogenous constituents of, lecithin, 922; cephalin.....	1375
Bread, digestibility of (I) salivary digestion <i>in vitro</i> .....	1245
Butyl alcohol, action of aqua regia on.....	1816
Butyl bromides, rearrangement of iso-, into tertiary.....	653
Butylchloral alcoholate, mol. wt. of some, in benzene soln.....	2533
Butylmalonic acid, cond. in abs. EtOH, 125; $\text{NH}_4$ salt of.....	1799
Butyl mercaptans, esterification of benzoic acid by isomeric.....	2757
1,3,5-Butylxylene, chlorination of.....	1812
<b>CADMIUM</b> , revision of at. wt. of (IV) electrolytic detn. of Cd in $\text{CdBr}_2$ .....	857
Cadmium bromide, detn. of Cd in.....	857
Caesium. See <i>Cesium</i> .	
Caffeine, action of aqua regia on.....	1817
Calcium, influence Ca ion upon ferri-ferrocyanide potential, 1928; estn. in ash of forage plants and animal carcasses.....	1996
Calcium carbonate, complete solubility curve of.....	975
Calcium chloride efficiency as drying agent.....	2038
Calcium oxide system: $\text{CaO}-\text{Al}_2\text{O}_3-\text{MgO}$ .....	568
Calcium sulfate soly. in $\text{AcONH}_4$ soln. at $25^\circ$ and criticism of present methods for sepn. of the sulfates of Ba, Sr, Ca and Pb by means of $\text{AcONH}_4$ solns.....	310
Calcium tartrate, crystn. of.....	2519
Calorimeter, adiabatic.....	1473
Camphoric acid, cond. in abs. EtOH.....	127
Capric acid, $\text{NH}_4$ salt of.....	1793
Caprylic acid, $\text{NH}_4$ salt of.....	1793
Carbamide, action of aqua regia on.....	1817
Carbon dioxide, specific cond. of pure $\text{H}_2\text{O}$ in equil. with atmospheric.....	1480
Carbonic acid, detn. of, combined and free, in soln. particularly in natural waters.....	947
Carcass, estn. of Ca in ash of animal.....	1996
Carnations, effects of large applications of commercial fertilizers on.....	2784
Carnaubic acid in alfalfa seed oil.....	485
Catalysis with weak acids, 901; studies on (I) addition compds. of esters with org. acids, 1712; decompn. of $\text{H}_2\text{O}_2$ in certain nonaqueous solns.....	1956, 2145
Cathode, occlusion of H by Pd.....	2577
Cellose, optical rotatory powers of some acetylated derivs. of maltose, and lactose.....	1867
Cells, voltaic for detg. H-ion concn., 936; calomel standard.....	20, 889
Cephalin brain.....	1375
Cerium, 42; vol. detn. by means of $\text{KMnO}_4$ .....	66
Cesium formate, behavior in (anhydrous) formic acid.....	271
Cesium halides, changes in vol. upon soln. in water of, 70; densities and cubical coeffs. of expansion of.....	259
Chamaecyparissobtusa, essential oil of, wood.....	699
Chemical compounds, color of.....	783
Chemical Constitution and Physiological Action (Spiegel, book review), 165; theories of.....	2225
Chemistry, Lab. Exercises Arranged to Accompany "First Course in Chemistry" (McPherson, Henderson, book review), 168; Practical Elementary (McFarland, book review), 487; in High School (Schoch, book review), 1437; Annual Reports of Progress of, for 1915 (book review).....	2576
Chemistry, Agricultural, Journal of Assoc. of Official Agricultural Chemists (book review).....	736
Chemistry, Biological, Practical Org. and Biochemistry (Plimmer, book review), 164; Physiological Chemistry (Mathews, book review), 165; Quant. Laws in (Arrhenius, book review), 939; Lab. Course in Org. and (Lothrop, book review).....	1905
Chemistry, Inorganic, Text-book of (Friend, book review), 730; Lab. Manual of, for Colleges (Newell, book review).....	2813

Chemistry, Mineralogical, Handbuch der Mineralchemie (Doelter, <i>et al.</i> , book review).....	732
Chemistry, Organic, Practical Org. and Biochemistry (Plimmer, book review), 164; Lab. Course in, and Physiological Chemistry (Lothrop, book review).....	1905
Chemistry, Physical, Introduction to Principles of, from Standpoint of Modern Atomistics and Thermodynamics (Washburn, book review), 944; Elements of (Jones, book review), 1144; Annuaire pour l'an 1916 (book review), 1260; Practical (Gray, book review), 1905; System of (Lewis, book review).....	2217
Chloral alcoholate, mol. wt. of some, in benzene soln. ....	2533
Chloral hydrate, action of aqua regia on.....	1817
Chloranil, prepn. of.....	1820
Chlorates, detn. of periodates, iodates, bromates and, in presence of each other.....	330
Chloric acid as reagent in org. chemistry.....	1079
Chlorides, equil. of $\text{HgCl}_2$ with other, 1272; dissociation tensions of certain hydrated, and vapor pressures of their satd. solns., 1439; in presence of thiocyanates, 1953; systematic sepn. of anions of group (I).....	2000
Chlorination with aqua regia—, of hydrocarbons.....	1809
Chlorine, interaction of H and, under influence of $\alpha$ -particles, 280; H and Cl ion activities of solns. of KCl in 0.1 molal HCl.....	1986
<i>p</i> -Chloroaniline, identification of.....	2725
<i>m</i> -Chlorobenzoic acid, cond. in abs. EtOH.....	126
Chlorobenzophenone, identification of.....	2724
Chlorocrotonic acid, $\text{NH}_4$ salt of.....	1796
Chloroform, action of aqua regia on.....	1817
Chlorofumaric acid, $\text{NH}_4$ salt of.....	1802
$\beta$ -Chlorolactic acid, $\text{NH}_4$ salt of.....	1791
Chloropentanes, hydrolysis of, as affected by high pressure.....	1368
<i>p</i> -Chlorophenyl- <i>p</i> -bromophenylphenylcarbinol.....	2078
<i>p</i> -Chlorophenyl- <i>p</i> -bromophenylphenylmethylamine hydrochloride.....	2100
<i>p</i> -Chlorophenyl- <i>p</i> -bromophenylphenylmethyl chloride.....	2079
<i>p</i> -Chlorophenyl- <i>p</i> -bromophenylphenylmethylhydroxylamine and hydrochloride.....	2079, 2080
<i>p</i> -Chlorophenyldiphenylmethylamine.....	2092
<i>p</i> -Chlorophenyl-diphenylmethylazide.....	2723
<i>p</i> -Chlorophenyldiphenylmethylchloroamine, rearrangement of.....	2093
<i>sym.-bis.-p</i> Chlorophenyl-diphenylmethylhydrazine.....	2733
<i>p</i> -Chlorophenyl-diphenylmethylhydrazine hydrochloride.....	2722
Chloropirrin, formation by action of aqua regia on org. substances.....	1813
Chlorotoluenes, action of Na methylate on products of nitration of <i>o</i> -, <i>p</i> - and <i>m</i> -.....	1327
Choline in brain lecithin.....	922
Chondrosamine pentacetates, isomeric.....	1431, 2216
Chromic acid, constitution of.....	1303
Chromium chlorides, dialysis of colloidal soln. of hydrous chromic oxide in $\text{CrCl}_3$ .....	1961
Chromium oxides, dialysis of colloidal soln. of hydrous chromic oxide in $\text{CrCl}_3$ .....	1961
Chromyl chloride, action on P trihalides.....	1923
Cinchona alkaloids, rates of conversion of stereoisomeric, into their toxins.....	901
Cinchonidine, conversion rate to cinchotoxine.....	904
Cinchonine, conversion rate to cinchotoxine.....	904
Cinchotoxine.....	903, 904
Cinnamic acid, cond. in abs. EtOH.....	127
Citric acid, modification of Pratt method for detn. of.....	2193
Cleveite, density of radio-lead from pure Norwegian.....	1658
Cobaltamines, studies on (I) various ionization types as detd. by f. p. lowering in aqueous soln., together with conductance measurements.....	2643
Cobalt chloride, dissociation tensions of hydrated, and vapor pressure of satd. solns. of the same.....	1439
Cobaltcyanides of rare earths.....	1497
Cobalt salts, detection of Ni in.....	1705
Colloid-chemistry, oxidation and reduction without addition of acid (II) reaction between $\text{SnCl}_4$ and $\text{K}_2\text{Cr}_2\text{O}_7$ , 47; Handbook of (Ostwald, book review).....	733
Colloids, effect of freezing on certain inorg. hydrogels, 588; solid solns., 613; dialysis of colloidal soln. of hydrous chromic oxide in $\text{CrCl}_3$ , 1961; colloidal arsenates and phosphates of Fe, 1970; theory of.....	1982
Color of chem. compds.....	783
Colorimetry, possible source of error in.....	716
Compressibility of certain typical hydrocarbons, alcohols and ketones.....	989
Condition equation, equation of state for gases and liquids.....	528

Conductivity, electric, of certain org. acids in abs. EtOH, 121; behavior of alkali metal formates in (anhydrous) formic acid, 271; extrapolation of values, 788; of solns. of certain iodides in isoamyl and propyl alcs., 1178; of solns. at different frequencies, 2396, 2403, 2415; measurement of (I) theory of design of cond. cells.....	2431
Conductivity cells, theory of design of.....	2431
Conductivity water, prepn. of.....	2460
Copper, estn. of, 884; accuracy of, voltmeters, 1156; bottle for iodimetric titration of, 1308; detn. of.....	1668
Copper chlorides, dissociation tensions of hydrated CuCl <sub>2</sub> and vapor pressure of satd. solns. of the same.....	1439
Copper compounds, spectrophotometric study of Cu complexes and biuret reaction.....	457
Copper sulfate, density of aq. solns. of, and H <sub>2</sub> SO <sub>4</sub> , 1021; basic.....	1947
Copper-tin group, electro-analytical method for detn. and sepn. of metals of.....	1660
Cottonseed oil, partition of lower alcohols between H <sub>2</sub> O and.....	2316
Coumaric acid, formation of.....	450
Coumarin, some derivs. of.....	446
Cresols, action of aqua regia on <i>p</i> -, <i>m</i> - and <i>o</i> -.....	1818, 1819
Crop rotation, presence of nitrites and NH <sub>3</sub> in diseased plants—its significance with regard to.....	2572
Crucible "fork".....	1203
Cryoscopy, measurements at low temps.....	615
<i>Cryptomeria japonica</i> , essential oil of leaves of.....	687
Crystallization, effect of dissolved substances on velocity of, of water, 317; effect of dissolved substances on velocity of, of H <sub>2</sub> O—(II) existence of hydrates in soln. as explanation of retarding effect of solute on velocity of crystn. of H <sub>2</sub> O, 1161; structure of, 2222; structure from viewpoint of chem. theory.....	2230
Crystals, forces between atoms in.....	2235
Cyanamides, synthesis of amidines from.....	2768
Cyanides, systematic sepn. of anions of group (I).....	2000
Cyanoacetic acids, alkyl.....	909
Cyan radical, action of the Grignard reagent on compds. contg.....	2768
Cyclopentadiene series, studies in.....	2535
Cyclopentadienodihydropyridazines, formation of.....	2535
<i>p</i> -Cymene monocarboxylic acids, synthesis of, together with certain of their derivs.....	1349, 1904
<b>D</b>	
<b>DATURIC ACID</b> in alfalfa seed oil.....	485
Density, floating equil., 1000; supposed effect of form of container on, of a gas, 1017; of aq. solns. of CuSO <sub>4</sub> and H <sub>2</sub> SO <sub>4</sub> .....	1021
Dialysis, temp. effect in, 1270; studies in (I) dialysis of colloidal soln. of hydrous chromic oxide in CrCl <sub>3</sub> .....	1961
Dialyzer, inexpensive, for class use, 1204; simple rapid.....	1270
1,3-Diamines, synthesis by reduction of 2-mercapto-6-oxypyrimidines.....	1854
<i>p</i> -Diaminodiphenylamine, action of aqua regia on.....	1818
2,4-Diaminophenol, action of aqua regia on.....	1818
Diaminophenoltetrachlorophthalein and dihydrochloride.....	2494, 2495
Diarylhydrazines, thermal decompn. of symmetrical.....	1736
Dibenzyl, chlorination of.....	1812
Dibromodinitrophenoltetrachlorophthalein.....	2493
3,5-Dibromo-4-hydroxybenzhydrol.....	1215
$\gamma$ , $\gamma$ -Dibromo- $\gamma$ -nitro- $\beta$ -phenyl- $\alpha$ -bromobutyrophenone.....	897
$\gamma$ , $\gamma$ -Dibromo- $\gamma$ -nitro- $\beta$ -phenylbutyrophenone.....	895
Di- <i>p</i> -bromophenylphenylmethylhydroxylamine and hydrochloride.....	2077
Dibromopyrocatechindisulfonic acid and salts.....	680
Dibromosuccinic acid, cond. in abs. EtOH, 125; NH <sub>4</sub> salt of.....	1801
2,4-Dichloroaniline, action of aqua regia on.....	1819
2,4-Dichloroazobenzene.....	1748
2,4-Dichlorohydrazobenzene, velocity of decompn. of.....	1753
Di- <i>p</i> -chlorophenylphenylmethylamine hydrochloride.....	2096
<i>p</i> -Dichlorophenylphenylmethylchloroamine.....	2097
Di- <i>p</i> -chlorophenylphenylmethylhydroxylamine.....	2074
Dichlorophthalic acid, cond. in abs. EtOH.....	127
Di- <i>p</i> -cymyl-[ <i>bb</i> ]-furodiazoles.....	1359, 1365
$\alpha$ , $\alpha'$ -3,3'-Di- <i>p</i> -cymyl- <i>N</i> -phenyl-[ <i>bb</i> ]-pyrroldiazole.....	1366
<i>p</i> -Diethylaminobenzhydrol ethyl ether.....	1209
Diethylamino- <i>m</i> -hydroxybenzoyltetrachlorobenzoic acid and some of its derivs.....	2101

Diethyl ketone, action of aqua regia on.....	1817
Diethylmalonic acid, cond. in abs. EtOH.....	124
Diethylphenylbenzylammonium chlorate.....	1085
Diffusion of I in KI solns.....	253
Digestion, salivary, of bread <i>in vitro</i> .....	1245
Dihydronaphthoic acids, structure of.....	400, 419
Dilution, free energy of, and f. p. lowerings in solns. of some salts of various types of ionization, and of salt mixts.....	2658
<i>p</i> -Dimethylaminobenzhydrol, reactions with Br, HNO <sub>2</sub> and HNO <sub>3</sub> .....	1208, 1209
Dimethyldiisopropyl dibenzoylhydrazines.....	1358, 1365
Dimethylethylcarbinol, action of oxalyl chloride on.....	2518
Dimethylmalonic acid, NH <sub>4</sub> salt of.....	1798
1,4-Dimethyl-6-nitro-2,3-cyclopentadieno-1,4-dihydropyridazine.....	2540
Dimethylphenylbenzylammonium chlorate.....	1085
3,6-Dimethyl-4,5-pyridazinedicarboxylic acid.....	2541
Dimethyl sulfate, utilization of hypochlorite color reactions in establishing mechanism of action of, on aniline.....	2507
5,5-Dimethyl-3-R-2-thiohydantoin.....	2523
1,3,5-Dinitrobenzoic acid, cond. in abs. EtOH.....	126
Dinitrobenzole urea.....	1611
Dinitrophenoltetrachlorophthalein and derivs.....	2489
Dinitropyrocolls, constitution of the 3 symmetrical.....	1065
Diphenylamine, action of aqua regia on.....	1818
1,4-Diphenyl-6-nitro-2,3-cyclopentadienodihydropyridazine.....	2544
Dipropylmalonic acid, cond. in abs. EtOH, 125; NH <sub>4</sub> salt of.....	1798
Dissociation of hydrogen into atoms, 1145; of solids and kinetic interpretation of phase rule.....	2263
Dissociation tensions of certain hydrated chlorides and the vapor pressures of their satd. solns.....	1439
Dissociation theory, modification of electrolytic.....	57
Dissolution, changes in vol. on, in water of the halogen salts of alkali metals (II), 70; bath used for, of samples in O-free atm.....	374
Drop weight method for detn. of surface tension.....	228
Drying agents, efficiency of CaCl <sub>2</sub> , NaOH and KOH as.....	2038
Dysprosium.....	45
<b>ELECTRODES</b> , lead, 792; convenient dip, 652; study of 0.1 N HCl-calomel, 2310; potential of Hg, against mercurous ion, 2356; effect of pressure on potential of H.....	
Electrons, effect of gases on, emission from heated metals as evidence of presence of stable absorbed films.....	2278
Elements, periodic system and properties of, 169; <i>Electrische Spectroanalyse Chemischer Atome</i> (Stark, book review).....	732
Energy, free, of HCl in aq. soln., 737; free, and heat capacity.....	2629, 2631
Enzyme action, studies on—corrections, 921; starch as substrate for.....	1885
Enzymes, certain conditions which affect activity of proteolytic, in wheat flour.....	1098
Equation of state. See <i>Condition equation</i> .	
Erbium, sepn. from Yt.....	1198
Erucic acid, NH <sub>4</sub> salt of.....	1797
Esterification, studies in.....	2746, 2757
Esters, action of salts with and without water of hydration on velocity of sapon. of, 105; sapon. of, 888; catalysis (I) addition compds. of, with org. acids.....	1712
Ethyl alcohol, conductivities of certain org. acids in abs., 121; <i>Alcoholometric Tables</i> (Thorpe, book review), 163; oxidation by means of KMnO <sub>4</sub> , 375; viscosity of certain solns. in, 833; partition between H <sub>2</sub> O and cottonseed oil, 2316; detn. in fermentation mixts.....	2561
Ethylbenzene, chlorination of.....	1811
Ethyl-di-(4-dimethylaminophenyl) carbinol.....	1210
Ethylene, action upon AlCl <sub>3</sub> .....	1384
Ethylenediamine chlorate.....	1083
Ethylmalonic acid, cond. in abs. EtOH.....	124
Ethyl mercaptan, esterification of <i>o</i> -, <i>m</i> - and <i>p</i> -toluic acids by.....	2746
Eudiometer, improvement of Hoffman's.....	1203
Europium.....	45
Euthamia caroliniana, volatile oil of (L) Greene.....	1398
<b>FATTY ACIDS</b> in alfalfa seed oil, 480; brain cephalin.....	
Feeding, Feed and (Henry, Morrison, book review).....	942

Feeding stuffs and Feeding (Henry, Morrison, book review), 942; nonprotein nitrogenous constituents of, 1425; estn. of Ca in ash of forage plants.....	1996
Fermentation mixtures, detn. of alcohol in.....	2561
Ferrieyanide, influence of K ion and of Ca ion upon ferri-ferrocyanide potential, 1928; systematic sepn. of anions of group I.....	2000
Ferrocyanide, influence of K ion and of Ca ion upon ferri-, potential, 1928; systematic sepn. of anions of group I.....	2000
Fertilizers, effects on large applications of commercial, on carnations.....	2784
Floating equilibrium.....	1000
Flour, certain conditions which affect activity of proteolytic enzymes in wheat.....	1098
Food from Sanitary Standpoint (Woodman, Norton, book review), 735; Analysis, Typical Method and Interpretation of Results (Woodman, book review), 941; Changes in, Supply and their Relation to Nutrition (Mendel, book review).....	1437
Formamides, reactions of—pyrazolone derivs., 1510; reactions.....	1841
Formic acid, behavior of alkali metal formates in (anhydrous).....	271
Freezing effect on certain inorg. hydrogels.....	588
Freezing point, free energy of dilution and, lowerings in solns. of some salts of various types of ionization, and of salt mixts., 2658; lowerings in aq. solns. of salts and mixts. of salts and of salt with nonelectrolyte.....	2676
Fumaric acid, cond. in abs. EtOH.....	125
Furfural, comparison of barbituric acid, thiobarbituric acid and malonylguanidine as quant. precipitants for.....	2156
Fusel oil, synthetic.....	1368
<b>GADOLINITE</b> , extn. of Be from.....	875
Gadolinium.....	45
Gadolinium sodium sulfate.....	873
Galactose pentacetate, fourth cryst., and some related compds.....	1223
Galactose tetracetate.....	1223
Gallic acid, action of aqua regia on.....	1820
Gases, equation of state for, 528; supposed effect of form of container on density of, 1017; adsorption by solids.....	2267
Gentiobiose, rotation of.....	1569
German Chem. (Phillips, book review).....	161
Ginger oil, zingiberol in.....	430
$\alpha$ -Glucosheptose hexacetates, isomeric.....	1575
Glucosamine pentacetates, isomeric.....	1431, 2216
Glucose, role of atm. O in oxidation of, with $\text{KMnO}_4$ in presence of varying amts. of alkali—products of oxidation, 150; effects of commercial, when fed to white rats, 930; action of aqua regia on, 1817; products of action of certain amylases on sol. starch, with special reference to formation of.....	1877
Glycerol, action of aqua regia on.....	1816
Glycol, action of oxalyl chloride on.....	2518
Glycolic acid, $\text{NH}_4$ salt of.....	1788
Grignard reagent, action on CN compds.....	2768
Guanidine, action of aqua regia on.....	1817
Guanidine chlorate.....	1683
<b>HALOGENATION</b> , chloric acid as reagent in org. chemistry.....	1079, 1809, 1813, 2545, 2736
Halogens, detection and detn. in org. compds., 711; and their Allies (Martin, Lancaster, book review).....	730
Heat capacity, free energy and.....	2629, 2631
Hen, distribution of urea in the blood and tissues of.....	1615
Hexahydropyrimidine, hydrolysis of.....	2466
Hexamethylenetetramine, action of aqua regia on.....	1817
Hinoki wood, essential oil of.....	699
Hippuric acid, quant. detn. in urine, blood, muscles and liver.....	2188
Holmium.....	45
Hydantoins, synthesis of phenylalanylglycinhydantoin.....	1087
Hydrates, action on the velocity of sapon. of esters.....	105
Hydrazine, oxidation of (VII) role of $\text{HNO}_2$ in formation of $\text{HN}_3$ .....	285
Hydrazine hydrate, action of bromopropionic acid on.....	1782
Hydrazines, attempts to rearrange unsymmetrical.....	2735
Hydrazino diacids.....	1771
Hydrazobenzene, thermal decompn. products of asymmetrical, 1750; effect of mol. H on.....	1760



Hydrazones, attempts to rearrange unsymmetrical.....	2735
Hydrazopropionic acid, ethyl ester of.....	1783
Hydrobromic acid, reaction between alcs. and aq. solns. of.....	1071
Hydrocarbons, compressibility of certain typical, 989; chlorination of, 1809; bromination by means of Br and HNO <sub>3</sub> .....	2545
Hydrochloric acid, free energy of, in aqueous soln., 737; reaction between alcs. and aq. solns. of, 1071; study of 0.1 N, calomel electrode.....	2310
Hydrocoumarinsulfonic acid, salts of.....	447, 449
Hydrocyanic acid, detn. of small quantities of.....	1230, 1645
Hydrofluoric acid, use in sepn. of heavy metals from Sn, Sb, W and Mo by means of elec. current.....	640
Hydrogels, effect of freezing on certain inorg.....	588
Hydrogen, interaction of, and Cl under influence of $\alpha$ -particles, 280; dissociation of, into atoms, 1145; effect of pressure on potential of, electrode, 2391; occlusion by Pd cathode.....	2577
Hydrogen ion, cell for detg. concn., 936; new and sensitive indicator for detn. of concns. between limits of 6 and 8 on the Sorensen scale, 1606; and chlorine ion activities of solns. of KCl in 0.1 molal HCl.....	1986
Hydrogen peroxide, partition coeffs. of, between water and org. solvents, 633; catalytic decompn. of, in certain nonaqueous solns.....	1956
Hydrogen sulfide, action on arsenic acid.....	52
Hydrolimettin sodium sulfonate.....	452
Hydronitric acid, role of HNO <sub>2</sub> in formation of.....	285
Hydroxybenzal- $\beta$ -phenylethylamine.....	384, 385
<i>p</i> -Hydroxybenzhydrol.....	1212
<i>p</i> -Hydroxybenzoic acid, action of aqua regia on.....	1818
<i>o</i> -Hydroxybenzylidenehydrazinodiacetic acid, monopotassium salt.....	1779
Hydroxybenzyl- $\beta$ -phenylethylamines.....	384, 385
Hydroxyisobutyric acid, cond. in abs. EtOH.....	124
Hydroxylamine hydrochloride, electrolytic prepn. of.....	2042
<b>I MINOACETIC-PROPIONIC ACID</b> , hydrochloride of.....	1780
Indicators, study of, for detn. of temporary hardness in water, 877; new and sensitive, for acidimetry and alkalimetry, and for detn. of H-ion concns. between limits of 6 and 8 on the Sorensen scale, 1606; sulfonphthalein series of.....	2772
Invertase, influence of certain substances on activity of, 722; adsorption of.....	1109
Iodates, detn. of periodates, bromates, chlorates and, in presence of each other.....	330
Iodides, conductance of solns. of certain, in isoamyl and propyl alcs., 1178; systematic sepn. of anions of group I.....	2000
Iodimetry, differential, 330; decompn. of tetrathionates in alk. soln. as source of error in.....	625
Iodine, diffusion in KI solns..... 253; source of error in certain titrations, 625; soly. in EtO-CCHCl <sub>3</sub> solns.....	1243
Iodoantipyrine periodide.....	2166
$\beta$ -Iodopropionic acid, NH <sub>4</sub> salt of.....	1791
Iodoxybenzene.....	1085
Iodoxyesitylene.....	1086
Iodoxytoluenes, <i>o</i> - and <i>p</i> -.....	1086
Iodoxyxylenes.....	1086
Ionization, theory of multiple, 57; cobaltammines (I) various, types as detd. by f. p. lowering in aq. soln., together with conductance measurements, 2643; free energy of dilution and f. p. lowerings in solns. of some salts of various types of, and of salt mixts., 2658; and solubility relations of salts of higher types.....	2679
Ions, app. for detg., in soln., 1711; intermediate, in solns. of uni-bivalent salts, and of lanthanum iodate.....	2679
Iron, anodic, relations of passive—polarization potentials as influenced by external gas pressures, 362; estn. of.....	884
Iron arsenate, colloidal.....	1970
Iron chlorides, oxidation-reduction reactions without the addition of acid—FeCl <sub>3</sub> and KMnO <sub>4</sub> .....	2607
Iron oxide, prepn. of colloidal hydrous ferric oxide.....	2607
Iron oxides, effect of freezing on ferric oxide hydrogels, 588; solid soln. in system Fe <sub>2</sub> O <sub>3</sub> -Fe <sub>3</sub> O <sub>4</sub> , 807; dissociation of Fe <sub>3</sub> O <sub>4</sub> in air.....	1188
Iron phosphates, colloidal.....	1970
Isoamyl alcohol, conductance of solns. of certain iodides in, 1178; partition between H <sub>2</sub> O and cottonseed oil, 2316; action of oxalyl chloride on.....	2517
Isoamyl bromide, influence of some solvents on rate of action of Na with.....	1128

Isobutyl alcohol, action of aqua regia on, 1816; partition between $H_2O$ and cottonseed oil, 2316; action of oxalyl chloride on.....	2517
Isobutyl bromide, rearrangement of, into tertiary butyl bromide.....	653
Isopropyl alcohol, action of aqua regia on.....	1816
Isopropyl-malonic acid, $NH_4$ salt of.....	1798
Isothiocyanates, thiocyanates and.....	1550, 1860
Isothiocyanacetic acid, Et ester of.....	1550
Itaconic acid, cond. in abs. EtOH.....	126
<b>JAMBUL</b> , some constituents of.....	2805
<b>KETONES</b> , compressibility of certain typical.....	989
Kinetics of heterogeneous reaction.....	2286
Kinetic Theory (Lewis, book review).....	2217
Kjeldahl method, comparative study of aeration and heat distn. in, for detn. of N.....	916
<b>LABORATORY</b> exercises, Arranged to Accompany "First Course in Chemistry" (McPherson, Henderson, book review).....	168
Lactose, optical rotatory powers of some acetylated derivs. of maltose, cellose and.....	1867
Lanthanum.....	44
Lanthanum iodate, intermediate ions in solns. of uni-bivalent salts, and of.....	2679
Lauric acid, $NH_4$ salt of.....	1793
Lead, density of, from radioactive minerals, 221; electrode, 792; density of radio-, from pure Norwegian cleveite, 1658; detn. of, 1673; at. wt. of, of radioactive origin,.....	2613
Lead acetate, factors controlling reactions of $Pb(NO_3)_2$ and, with $Na_2HAsO_4$ .....	2014
Lead arsenates.....	2014, 2027, 2366
Lead bromide, density and cubical coeff. of expansion of.....	266
Lead chloride, density and cubical coeff. of expansion of.....	266
Lead iodide, thermodynamic properties of.....	2295
Lead monoxide, equil. in system: $PbO$ , $As_2O_3$ , $H_2O$ .....	2366
Lead nitrate, factors controlling reactions of, and lead acetate with $Na_2HAsO_4$ .....	2014
Lead sulfate, soly. in $AcONH_4$ soln. at $25^\circ$ and criticism of present methods for sepn. of the sulfates of Ba, Sr, Ca and Pb by means of $AcONH_4$ solns.....	310
Lecithin, nitrogenous constituents of brain.....	922
Life process, Temperatur und Lebensvorgänge (Kanitz, book review).....	167
Lime-sulfur, estn. of thiosulfate S in, solns. by I titration.....	1701
Limettin.....	451
Linoleic acid in alfalfa seed oil, 484; in alfalfa seed oil.....	484
Liquids, app. for detn. of surface tension at interface between two, 236; surface tension at the interface between two, 242; equation of state for, 528; properties of mixed, 555; properties of mixed, 844; supersatd. solns. of, in, 1166; constitution and fundamental properties of, 2221; solubilities of, in liquids.....	2316
Lithium, sepn. from other alkali metals.....	2326
Lithium ethylate, reaction of MeI with, at $0^\circ$ .....	2145
Lithium formate, behavior in (anhydrous) formic acid.....	271
Lithium halides, changes in vol. upon soln. in water of.....	70
Liver, detn. of hippuric acid in.....	2188
<b>MAGNESIUM</b> , action on solns. of KCl.....	2594
Magnesium chloride, dissociation tensions of hydrated, and vapor pressures of satd. solns. of the same.....	1439
Magnesium oxide, system: $CaO-Al_2O_3-MgO$ .....	568
Maleic acid, cond. in abs. EtOH.....	125
Malonic acid, cond. in abs. EtOH.....	124
Malonylguanidine, comparison of barbituric acid, thiobarbituric acid and, as quant. precipitants for furfural.....	2156
Maltose, action of aqua regia on, 1816; optical rotatory powers of some acetylated derivs. of, cellose and lactose.....	1867
Mandelic acid, cond. in abs. EtOH.....	127
Manganese, oxidation of, solns. in presence of air.....	638
Manninotriose, rotation of.....	1569
Mechanics, Thermodynamics and Statistical (Lewis, book review).....	2217
Melibiose, rotation of.....	1568
Menthol, action of oxalyl chloride on.....	2518

Menthylamine chlorate.....	1083
2-Mercapto-6-chloropyrimidines, reduction of.....	1385
2-Mercapto-6-oxypyrimidines, synthesis of 1,3-diamines by reduction of.....	1854
2-Mercaptopyrimidines, mechanism of action of Br on.....	1557
Mercurous ion, potential of Hg electrode against.....	2356
Mercury, potential of, electrode against mercurous ion.....	2356
Mercury chlorides, dissociation pressures of HgCl, 801; calomel standard cell, 20, 889; equilibria of HgCl <sub>2</sub> with other chlorides, 1272; study of 0.1 N HCl-calomel electrode.....	2310
Mesaconic acid, cond. in abs. EtOH.....	126
Metals, effect of gases on electron emission from heated, as evidence of presence of stable absorbed films.....	2278
Methacetin, periodides of.....	140
<i>p</i> -Methoxybenzal- $\beta$ -phenylethylamine.....	384
<i>p</i> -Methoxybenzhydrol.....	1213
Methoxybenzhydrol ethyl ether.....	1214
<i>p</i> -Methoxybenzyl- $\beta$ -phenylethylamine.....	384
3-Methoxy-4-hydroxybenzal- $\beta$ -phenylethylamine.....	386
3-Methoxy-4-hydroxybenzyl- $\beta$ -phenylethylamine.....	386
Methyl alcohol, viscosity of certain solns. in, 833; detn. of acetone in systems of, H <sub>2</sub> O and KF, 1136; partition between H <sub>2</sub> O and cottonseed oil.....	2316
Methylbenzylidenaminohydantoic acid.....	1784
Methylethylenediamine, synthesis of.....	2135
Methyl ethyl ketone, equil. in systems of H <sub>2</sub> O, inorg. salts and, 1136; action of aqua regia on.....	1817
$\beta$ -Methyl fructoside, cryst., and its tetracetate.....	1216
Methyl iodide, reaction with Na, K and Li ethylates at 0°.....	2145
Methylisopropylhippuric acids and Et ester.....	1357, 1367
$\gamma$ -Methyl- $\gamma$ -nitro- $\beta$ -phenyl- $\alpha$ -bromovalerophenone.....	900
$\gamma$ -Methyl- $\gamma$ -nitro- $\beta$ -phenylvalerophenone.....	899
Methyl orange, action of aqua regia on.....	1819
Methyl-1-phenyl-2-anisoyltrimethylenedicarboxylic acid.....	1523
Methylphenyl-(3-bromo-4-dimethylaminophenyl)carbinol.....	1211
2-Methyltetraabromobenzacetimidazole.....	687
Methyltriphenylmethylchloroamine, attempts to rearrange.....	2090
Microscope, petrographic, in analysis.....	1647
Mineralogy, Handbuch der Mineralchemie (Doelter, <i>et al.</i> , book review).....	732
Minerals, density of Pb from radioactive.....	221
Molecular rearrangements, theory of, 2046; of triarylmethylazides, 2718; of <i>sym.-bis.-triarylmethyl-</i> methylhydrazines.....	2727
Molecules, the atom and.....	762
Molybdenum, use of HF in sepn. of heavy metals from, by means of elec. current.....	640
Monazite sand, sepn. of rare earths giving the more sol. double sulfates from Brazilian.....	41
Morphine, quant. detn. of, in various organs when injected into cats and rabbits.....	1873
Muscles, detn. of hippuric acid in.....	2188
Myristic acid, NH <sub>4</sub> salt of.....	1794
<b>NAPHTHOLS</b> , action of aqua regia on $\alpha$ - and $\beta$ -.....	1820
Naphthyl-(4-dimethylaminophenyl) carbinol.....	1210
Neodymium, 45; at. wt. of.....	302
Neodymium chloride, density and cubical coeff. of expansion of.....	266
Neodymium cobalticyanide.....	1497
Neurokeratin, compn. of.....	2558
New books. See <i>Books, new (Reviews)</i> .	
Nickel, detection in Co salts.....	1705
Nickel chlorides, dissociation tensions of hydrated, and vapor pressure of satd. solns. of the same.....	1439
Nitriles, prepn. of, (II) prepn. of aliphatic nitriles, 2120; prepn. of, (III) catalytic prepn. ....	2128
Nitrites, titrametric detn. of, 1683; presence in diseased plants—its significance with regard to crop rotation and soil depletion.....	2572
Nitroamines, application of nitrometer for detn. of constitution and estn. of N in.....	2552
<i>m</i> -Nitroaniline, action of aqua regia on.....	1819
<i>m</i> -Nitrobenzoic acid, cond. in abs. EtOH.....	126
Nitro compounds, addition of aliphatic, to unsatd. compds., 889; application of nitrometer for detn. of constitution and estn. of N in a class of.....	2552
Nitro-fibroin, hydrolysis with HCl.....	1392
Nitrogen, comparative study of aeration and heat distn. in Kjeldahl method for detn. of, 916;	

- non-protein, of feeding stuffs, 1425; application of nitrometer for detn. of constitution and estn. of, in a class of nitro compds. (nitroamines), 2552; efficiency of aeration method for distg.  $\text{NH}_3$  in detg. N by the Kjeldahl method. . . . . 2568
- Nitrometer, application for detn. of constitution and estn. of N in a class of nitro compds. (nitroamines) . . . . . 2552
- 4-Nitro-5-methyl-2-sulfobenzoic acid, and some of its derivs. . . . . 1338
- Nitrophenols, action of aqua regia on . . . . . 1818, 1819
- o*-Nitrophenylacetic acid,  $\text{NH}_4$  salt of . . . . . 1786
- $\gamma$ -Nitro- $\beta$ -phenyl- $\alpha$ -bromobutyrophenone . . . . . 896
- $\gamma$ -Nitro- $\beta$ -phenyl- $\alpha$ -bromovalerophenone . . . . . 898
- $\gamma$ -Nitro- $\beta$ -phenylbutyrophenone . . . . . 893
- Nitrophenyl ethers, mono- . . . . . 1534
- $\gamma$ -Nitro- $\beta$ -phenyl- $\alpha$ -iodobutyrophenone . . . . . 896
- $\gamma$ -Nitro- $\beta$ -phenylvalerophenone . . . . . 897
- Nitrous acid, role in formation of  $\text{HN}_2$  . . . . . 285
- Nucleosides, secondary-pyrimidine-, and their unique behavior on hydrolysis . . . . . 1844
- Nutrition, changes in Food Supply and Their Relation to (Mendel, book review) . . . . . 1437
- OCCCLUSION**, of H by Pd cathode . . . . . 2577
- Oils, zingiberol in, of ginger, 430; of Sugi leaves, 687; of Formosan Hinoki wood, 699; of *Euthamia caroliniana* (L). Greene . . . . . 1398
- Oleic acid in alfalfa seed oil . . . . . 484
- Organic acids. See *Acids*.
- Organic compounds, mol., 702; detection and detn. of halogens in, 711; addition of aliphatic nitro compds. to unsatd. compds., 889; action of anhydrous  $\text{NH}_4\text{Cl}$  on unsatd. compds., 1382; see also *Aromatic compounds*.
- Organs*, reaction of pancreas and other . . . . . 1115
- Oscillaria prolifica, chem. compn. of . . . . . 1402
- Osmosis, relation of, of solns. of electrolytes to membrane potentials, 1029; of some solns. of electrolytes with porcelain membranes, and relation of osmose to membrane potential. . . . . 1036
- Osmotic pressure, of sucrose solns. at  $30^\circ$  . . . . . 1907
- Oxalic acid, action of soln. of KOH in alc. on esters of . . . . . 1803
- Oxalyl chloride, action on primary, secondary and tertiary alcohols . . . . . 2514
- Oxalylhydrazide, estn. by its interactions with halogens and halogen oxyacids . . . . . 2736
- Oxidation and reduction without addition of acid (II) reaction between  $\text{SnCl}_2$  and  $\text{K}_2\text{Cr}_2\text{O}_7$ , 47; role of atm. O in, of glucose with  $\text{KMnO}_4$  in presence of varying amts. of alkali—products of . . . . . 150
- Oxidation-reduction reactions without addition of acid . . . . . 2607
- Oxygen, role of atmospheric, in the oxidation of glucose with  $\text{KMnO}_4$  in the presence of alkali, 150; sodium pyrogallate as reagent for detn. of . . . . . 1687
- PALLADIUM**, occlusion of H by, cathode . . . . . 2577
- Pancreas, reaction of . . . . . 1115
- Paraffin, soly. in water . . . . . 1003
- Partition of lower alcohols between  $\text{H}_2\text{O}$  and cottonseed oil . . . . . 2316
- Partition coefficients of  $\text{H}_2\text{O}_2$  between  $\text{H}_2\text{O}$  and certain org. solvents . . . . . 633
- Passivity, anodic behavior of passive Fe . . . . . 362
- Peptides, spectrophotometric study of Cu complexes of . . . . . 457
- Periodates, detn. of iodates, bromates, chlorates and, in presence of each other . . . . . 330
- Periodic system and properties of elements, 169; Ueber das periodische System der chemischen Elemente (Bilecki, book review) . . . . . 732
- Periodides, org., (I) of phenacetin, methacetin and triphenin, 140; organic . . . . . 2166
- Petroleum, presence of  $\text{C}_6\text{H}_6$  homologs in high boiling distillates of . . . . . 393
- Pharmacognosy, Scientific and Applied (Kraemer, book review) . . . . . 162
- Phase rule, statement of, 983; dissociation of solids and kinetic interpretation of . . . . . 2263
- Phenacetin, periodide of . . . . . 140
- Phenol, properties of  $\text{PhOH-H}_2\text{O}$  and of  $\text{NEt}_3\text{-H}_2\text{O}$  mixts . . . . . 844
- Phenols, addition compds. of, with org. acids, 1309; catalytic decompn. of certain, silver salts . . . . . 1761
- Phenoltetrachlorophthalein, nitration products of, and some of their derivs . . . . . 2486
- Phenylacetic acid, cond. in abs. EtOH . . . . . 124
- sym.*-Phenylalanineglycineurea . . . . . 1096
- Phenylalanylglycine-hydantoin, synthesis of . . . . . 1087
- Phenylamidoacetic acid,  $\text{NH}_4$  salt of . . . . . 1787
- 1-Phenyl-2-anisoyltrimethylene-3,3-dicarboxylic acid . . . . . 1524

1-Phenyl-2-anisoyltrimethylene-3-monocarbonic acid.....	1532
Phenylbromoacetic acid, $\text{NH}_4$ salt of.....	1786
1-Phenyl-3,6-dimethyl-4-keto-1,4-dihydro-5-pyridazinecarboxylic acid.....	2542
2-Phenyl-1,4-dimethyl-6-nitro-2,3-cyclopentadienedihydropyridazine.....	2542
Phenylenediamines, action of aqua regia on.....	1819
<i>p</i> -Phenylenediamine chlorate.....	1681
Phenyl ethers, bibliography of.....	1547
$\beta$ -Phenylethylamine, formation of Schiff bases from, and their reduction to alkyl derivs. of this amine.....	381
Phenylhydrazine, action of aqua regia on.....	1819
Phenylmethylcarbinol, action of oxalyl chloride on.....	2518
Phenylpropionic acid, cond. in abs. EtOH.....	126
Phenyltolylcarbinol.....	1215
Phosphorus, black, 609; blackening of yellow.....	887
Phosphorus compounds in starch.....	472
Phosphorus trihalides, action of chromyl chloride on.....	1923
Phthalic acids, cond. in abs. EtOH.....	127
Physics, Elementes de física geral (Gomez, Machado, book review).....	939
Physiological action, Chem. Constitution and (Spiegel, book review).....	165
Picric acid, cond. in abs. EtOH.....	126
Piezometer.....	992
Pinacone, action of oxalyl chloride on.....	2519
Piperazine chlorate.....	1083
Pipet, double, for liquid reagents in gas analysis.....	1683
Plants, Soil Conditions and, Growth (Russell, book review), 944; estn. of Ca in ash of forage, 1996; presence of nitrites and $\text{NH}_4$ in diseased—its significance with regard to crop rotation and soil.....	2572
Plum, chem. changes occurring during ripening of wild goose plum.....	718
Poison ivy, constituents of.....	1421
Poison oak, poisonous principle of.....	1417
Polarization, anodic behavior of passive Fe—polarization potentials as influenced by external gas pressures.....	362
Polypeptide-hydantoin, synthesis of.....	1087
Potassium chloride, H and Cl ion activities of solns. of KCl in 0.1 molal HCl, 1985; action of Mg on solns. of.....	2594
Potassium dichromate, reaction between $\text{SnCl}_2$ and.....	47
Potassium ethylates, reaction of MeI with, at $0^\circ$ .....	2145
Potassium fluoride, detn. of acetone in systems of MeOH, $\text{H}_2\text{O}$ and.....	1136
Potassium halides, changes in vol. upon soln. in water of, 70; densities and cubical coeffs. of expansion of.....	259
Potassium hydroxide, action of a soln. of, in alc. on oxalic esters, 1833; efficiency, as drying agent.....	2038
Potassium iodide, diffusion of I in, solns.....	253
Potassium ion, influence on ferri-ferrocyanide potential.....	1928
Potassium permanganate, oxidation of EtOH by means of, 375; oxidation-reduction reactions without the addition of acid— $\text{FeCl}_2$ and.....	2607
Potential, electric, influence of K ion and of Ca ion on ferri-ferrocyanide potential, 1928; of Hg electrode against mercurous ion, 2356; effect of pressure on, of H electrode.....	2391
Potentiometer, practical installation of double combination.....	1266
Praseodymium.....	44
Pressure, influence on solubility.....	2632
Propiophenetidine hydriodo-diiodide.....	149
Propiophenetidine hydriodotetraiodide.....	150
Propyl alcohol, conductance of solns. of certain iodides in, 1178; action of aqua regia on, 1816; partition between $\text{H}_2\text{O}$ and cottonseed oil, 2316; action of oxalyl chloride on <i>N</i> -.....	2517
Propylmalonic acid, cond. in abs. EtOH.....	124
Proteins, spectrophotometric study of Cu complexes of, 457; nitrated.....	1392
Proteolysis, examn. of certain methods for study of proteolytic action.....	2199
Pump, device for regulating, used in exhausting vacuum oven.....	1063
Pyramidone periodide.....	2166
Pyrazolone derivs. of the formamidines.....	1510
Pyridine, action of aqua regia on.....	1870
Pyridine chlorate.....	1083
Pyrimidine-nucleosides, secondary, and their unique behavior on hydrolysis.....	1844
Pyrimidines, researches on.....	1385, 1557, 1844, 1854
Pyrogallal acid, action of aqua regia on.....	1820

<b>QUINAZOLINES</b> .....	1606
Quinoline, action of aqua regia on.....	1820
Quinoline chlorate, prepn. of.....	1084
Quinone-phenolate theory, sulfonphthalein series on indicators and.....	2772
<b>RADIO-LEAD</b> . See <i>Lead</i> .	
Raoult's Law.....	1452
Rare earth cobalticyanides.....	1497
Rare earths, sepn. of, giving the more sol. double sulfates from Brazilian monazite sand, 41; Their Occurrence, Chemistry and Technology (Levy, book review), 733; Industry (Johnstone, book review).....	734
$\alpha$ -Rays, Interaction of H and Cl under influence of.....	280
Reactions, Baly's theory of chem., 1, 15, 227; in non-aqueous solvents, 1923; of both the ions and non-ionized forms of acids, bases and salts—reaction of MeI with Na, K and Li ethylates at 0°, 2145; kinetics of heterogeneous.....	2286
Reactivity, Baly's theory of chem.....	1, 15, 227
Reduction, oxidation and, without addition of acid (II) reaction between SnCl <sub>2</sub> and K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> .....	47
Resorcinol, action of aqua regia on, 1820; colors produced by, in solns. of certain salts and use of these colors as means of detecting resorcinol in presence of other phenols.....	2182
Rhus diversiloba, poisonous principle of.....	1417
Rhus toxicodendron, constituents of.....	1421
Rubidium formate, behavior, in (anhydrous) formic acid.....	271
Rubidium halides, changes in vol. upon soln. in water of, 70; densities and cubical coeffs. of expansion of.....	259
<b>SACCHARIN</b> , action of aqua regia on.....	1820
Saliva, digestion of bread by, <i>in vitro</i> .....	1245
Salts, action of, with and without water of hydration on velocity of sapon. of esters, 105; equil. in systems of Me Et ketone, H <sub>2</sub> O and inorg., 1136; reaction of both ions and nonionized forms of acids, bases and, 2145; free energy of dilution and f. p. lowerings in solns. of some, of various types of ionization, and of salt mixts., 2658; freezing-point lowerings in aq. solns. of, and mixts. of salts and of salt with non-electrolyte, 2676; ionization and solubility relations of, of higher types, (IV) intermediate ions in solns. of uni-bivalent salts, and of lanthanum iodate, 2679; effect of, on solubility of other salts—solubility relations of very sol. bi-univalent salt.....	2709, 2714
Samarium.....	45
Saponification, action of salts with and without water of hydration on velocity of, of esters, 105; of esters.....	888
Schiff bases, formation from $\beta$ -phenylethylamine and their reduction to alkyl deriva. of this amine.....	381
Sebacic acid, cond. in abs. EtOH.....	125
Semicarbazide, estn. by its interactions with halogens and halogen oxyacids.....	2736
Semicarbazinodipropionic acid, ethyl ester of.....	1783
Semioxamazine, estn. by its interactions with halogens and halogen oxyacids.....	2736
Silica, hydrogels, 588; quant. detn. of.....	1050
Silver, electroanalysis of, with solns. of AgCl in NH <sub>3</sub> , 1682; inclusions in, voltameter.....	2044
Silver fulminate, stability under water.....	486
Silver iodide, thermodynamic properties of.....	2295
Silver salts, catalytic decompn. of certain phenol.....	1761
Silver voltameter, inclusions in, deposits.....	496
Sodium, influence of some solvents on rate of action of, with isoamyl bromide.....	1128
Sodium aci-nitrophenylbutyropheneone.....	893
Sodium arsenate, factors controlling reactions of Pb nitrate and Pb acetate with Na <sub>2</sub> HAsO <sub>4</sub> .....	2014
Sodium ethylate, reaction of MeI with, at 0°.....	2145
Sodium formate, behavior in (anhydrous) formic acid.....	271
Sodium gadolinium sulfate.....	873
Sodium halides, changes in vol. upon soln. in water of, 70; densities and cubical coeffs. of expansion of.....	259
Sodium hydroxide, efficiency as drying agents.....	2038
Sodium methylate, action on products of nitration of <i>o</i> -, <i>p</i> - and <i>m</i> -chlorotoluenes.....	1327
Sodium pyrogallate, as reagent for detn. of O.....	1687
Soils, Conditions and Plant Growth (Russell, book review), 944; Boden-Bakterien und Boden-Fruchtbarkeit (Löhnis, book review), 945; presence of nitrites and NH <sub>3</sub> in diseased plants—its significance with regard to depletion of.....	2572

Solids, constitution and fundamental properties of, 2221; sublimation of, 2249; adsorption of gases by.....	2267
Solubility of several substances in mixed nonaq., 1235, 1452; of liquids in liquids, 2316; influence of pressure on, 2632; ionization and, relations of salts of higher types, 2679; effect of salts on, of other salts—solubility relations of very sol. bi-univalent salts.....	2709, 2714
Solute, retarding effect of, on velocity of crystn. of $H_2O$ .....	1161
Solutions, vapor pressure of, 515; nonideal—activity of a difficultly sol. component, 626; viscosity of certain alcoholic, 833; supersaturated, of liquids in liquids, 1166; studies in measurement of elec. cond. of, at different frequencies, 2396, 2403, 2415; free energy of dilution and f. p. lowerings in, of some salts of various types of ionization, and of salt mixts., 2658; freezing-point lowerings in aq., of salts and mixts. of salts and of salt with non-electrolyte, 2676; see also <i>Dissolution</i> .	
Solutions, solid, in system $Fe_2O_3-Fe_3O_4$ .....	807
Solvents, solubilities of several substances in mixed nonaq. solns., 1235; reactions in non-aqueous.	1923
Spectroanalysis, <i>Electrische Spectroanalyse Chemischer Atome</i> (Stark, book review).....	732
Spectrophotometry, of Cu complexes and biuret reaction.....	457
Starch, phosphoric acid in, 472; action of aqua regia on, 1817; products of action of certain amylases upon sol., with special reference to formation of glucose, 1877; as substrate for enzyme action.....	1885
Strontium sulfate, soly. in $AcONH_4$ soln. at $25^\circ$ and criticism of present methods for sepn. of the sulfates of Ba, Sr, Ca and Pb by means of $AcONH_4$ solns.....	310
Strychnine, soly. in $Et_2O-CHCl_3$ solns.....	1242
Suberic acid, $NH_4$ salt of.....	1801
Sucrose, action of aqua regia on, 1816; osmotic pressure of, solns. at $30^\circ$ .....	1907
Sucrose groups, rotatory powers of sugars of.....	1566, 1570
Sugars, numerical relations among rotatory powers of compound, 1566, 1904; prepn. of bromoacetyl.....	2187
Sugi leaves, essential oil of.....	687
Sulfanilic acid, action of aqua regia on.....	1818
Sulfonphthalein series of indicators.....	2772
Sulfosalicylic acid, cond. in abs. $EtOH$ .....	126
Sulfuric acid, properties of $H_2SO_4-H_2O$ mixts., 555; density of aq. solns. of $CuSO_4$ and.....	1021
Sumbul root, constituents of.....	432
Supersaturation, solns. of liquids in liquids.....	1166
Surface tension, drop wt. method for detn. of, 228; app. for detn. of, at interface between 2 liquids, 236; at interface between two liquids and effect of acids, salts and bases on interfacial tension, 242; app. for detn. of, with metal thermoregulator.....	246
<b>TANNIC ACID</b> , action of aqua regia on.....	1820
Tartaric acid, action of aqua regia on, 1817; crystn. of Ca salt of.....	2519
Tautomerism, 1,4,5,6-tetrahydroxynaphthalene, 387, 1144; electronic, of benzene derivs., 1333; of triarylcannabinols.....	1577
Temperature, <i>Temperatur und Lebensvorgänge</i> (Kanitz, book review).....	167
Temperature, low, cryoscopic measurements at.....	615
Terbium.....	45
Ternary systems, $CaO-Al_2O_3-MgO$ .....	568
Tetraaminophenoltetrachlorophthalein.....	2497
Tetrabromo-o-phenylenediacetamide.....	685
Tetrabromo-o-quinone, derivs. of.....	676
$\beta$ -Tetracetyl methyl fructoside.....	1219
Tetrachloromethylmercaptopan, utilization of, for prepn. of alkyl isothiocyanates.....	1860
Tetrachloroquinone, formation by action of aqua regia on org. substances.....	1813
Tetraethylammonium chlorate.....	1084
1,4,5,6-Tetrahydroxynaphthalene.....	387, 1144
Tetramethylammonium chlorate.....	1084
Tetranitrophenoltetrachlorophthalein and derivs.....	2495
Tetraphenylethylene dichloride and derivs.....	707
Tetrapropylammonium chlorate.....	1084
Theobionates, decompn. in alk. soln. as source of error in certain I titrations.....	625
Theobromine, action of aqua regia on.....	1817
Thermodynamics, <i>Introduction to Principles of Physical Chemistry, from Standpoint of Modern Atomistics and</i> (Washburn, book review), 944; and <i>Statistical Mechanics</i> (Lewis, book review).....	2217
Thermoregulator, app. for detg. surface tension with a metal, for the quick adjustment of temp.....	

Thiazole, action of certain acid reagents on the substituted ureas and thiazole (II).....	1841
Thiazole derivs., of the formamidines.....	1841
Thiobarbituric acid, comparison of barbituric acid, and malonylguanidine as quant. precipitants for furfural, 2156; condensation of, with aromatic aldehydes.....	2164
Thiocyanates and isothiocyanates, 1550, 1860; chlorides in presence of, 1953; systematic sepn. of anions of group I, 2000; systematic detection of.....	2622
Thiodiglycolic acid, cond. in abs. EtOH.....	125
Thiosulfate, estn. of, S in lime-S solns. by I titration.....	1701
Tin, use of HF in sepn. of heavy metals from, by means of elec. current, 640; sepn. of As, Sb and, 1011; detn. of.....	1666
Tin chlorides, reaction between SnCl <sub>2</sub> and K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> .....	47
Tin group, sepn. of metals of.....	1011
Tissues, distribution of urea in, of certain vertebrates with especial reference to the hen.....	1615
Toluic acids, cond. in abs. EtOH of <i>o</i> - and <i>p</i> -, 127; esterification of <i>o</i> -, <i>m</i> - and <i>p</i> -, by ethyl mercaptan.....	2746
<i>p</i> -Toluidine, action of aqua regia on.....	1818
Toluidine chlorate, <i>o</i> - and <i>p</i> -.....	1080
Toxines, rates of conversion of stereoisomeric cinchona alkaloids into their.....	901
Trehalose groups, rotatory powers of sugars of.....	1571
Triarylcarbinols, tautomerism of.....	1577
Triarylmethylazides, molecular rearrangement of.....	2718
Triarylmethylchloroamines, mol. rearrangement of some.....	2095
<i>sym</i> - <i>bis</i> -Triarylmethylhydrazines, mol. rearrangement of.....	2727
Triarylmethylhydroxylamines, mol. rearrangement of.....	2069
Tribromoacetic acid, NH <sub>4</sub> salt of.....	1786
Tribromophenol, action of aqua regia on.....	1819
Tribromotertiary-butyl-alcohol, acetic ester of.....	2740
Trichloroacetic acid, addition compds. of esters with.....	1712
Trichlorobutyric acid, NH <sub>4</sub> salt of.....	1792
Trichlorodiethylaminooxanthonecarboxylic acid, and some of its derivs.....	2101
Trichlorophenol, action of aqua regia on.....	1819
Triethylamine, properties of -H <sub>2</sub> O mixts.....	814
Trihalogentertiary-butyl-alcohols, derivs. of.....	2740
Triiodophenol, silver salt of, and its catalytic decomps.....	2474
Trimethylcarbinol, action of oxalyl chloride on.....	2518
Trimethylene, reactions of some carboxyl derivs. of.....	1517
Trimethylene chlorohydrin, prepn. of.....	2481
Trimethylene oxide, studies of—(I) prepn. and characterization.....	2478
Trimethylsulfine chlorate.....	1085
Triphenin, periodides of.....	140
Triphenylcarbinol, action of oxalyl chloride on.....	2519
Triphenylmethyl.....	1577
Triphenylmethylazide.....	2721
Triphenylmethylbromoamine.....	2085
Triphenylmethylchloromethylamine.....	2089
Triphenylmethyldichloroamine.....	2088
Triphenylmethylhalogenamines, mol. rearrangement of.....	2081
<i>bis</i> -Triphenylmethylhydrazine, symmetrical.....	2720
Triphenylmethylhydrazine hydrochloride.....	2720
$\beta$ -Triphenylmethyl- $\beta$ -methylhydroxylamines, mol. rearrangements of.....	2046
1,2,4-Triphenyl-6-nitro-2,3-cyclopentadienodihydropyridazine.....	2544
Trypsin, assumed destruction of, by pepsin and acid.....	1620
Tungsten, use of HF in sepn. of heavy metals from, by means of elec. current.....	640
Tungsten derivatives, analysis of certain, 2377; new.....	2383
<b>UNSATURATED COMPOUNDS, addition of aliphatic nitro compds. to, 889; action of anhydrous AlCl<sub>3</sub> upon.....</b>	
Urea, distribution of, in blood and tissues of certain vertebrates with especial reference to the hen.....	1615
Ureas, action of certain acid reagents on the substituted, and thiazole (II).....	131
Uric acid, action of aqua regia on.....	1817
Urine, detn. of hippuric acid in.....	2188
<b>VACUUM OVEN, device for regulating pump used in exhausting.....</b>	
Vanadic acid, estn. of, after reduction by metallic Ag, 1297; reduction by HI.....	1063
Vanadium, electrometric titration.....	2369
	341



- Vapor pressure of solns.—lowering of, of water produced by dissolved KCl, 515; dissociation tensions of certain hydrated chlorides and the vapor pressures of their satd. solns. . . . . 1439
- Viscosity, sources of error in, measurement of, 27; of certain alcoholic solns. . . . . 833
- Vitiatine, structure of. . . . . 2135
- Voltameter, inclusions in silver, deposits, 496; accuracy of copper, 1156; inclusions in Ag. . . . . 2044
- Volume, changes in, on soln. in water of halogen salts of alkali metals (II). . . . . 70
- Vreeland oscillator, measurement of elec. cond. of solns. at different frequencies—(V) use of, and other sources of current for cond. measurements. . . . . 2396
- WASH BOTTLE**, non-spattering. . . . . 1502
- Water, effect of dissolved substances on velocity of crystn. of, 317; lowering of vapor pressure of, produced by dissolved KCl, 515; properties of  $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$  mixts., 555; from Sanitary Standpoint (Woodman, Norton, book review), 735; properties of phenol- $\text{H}_2\text{O}$  mixts., 844; indicators for detn. of temporary hardness in, 877; detn. of carbonic acid, combined and free, in soln. particularly in natural waters, 947; detn. of acetone in systems of MeOH, KF and, and equil. in systems of Me Et ketone,  $\text{H}_2\text{O}$  and inorg. salts, 1136; effect of dissolved substances on velocity of crystn. of, (II) existence of hydrates in soln. as explanation of retarding effect of solute on velocity of crystn. of  $\text{H}_2\text{O}$ , 1161; specific cond. of pure, in equil. with atmospheric  $\text{CO}_2$ , 1480; partition of lower alcohols between, and cottonseed oil, 2316; equil. in system  $\text{PbO}$ ,  $\text{As}_2\text{O}_5$ ,  $\text{H}_2\text{O}$ , 2366; prepn. of conductivity. . . . . 2460
- m*-**XYLENES**, chlorination of. . . . . 1809, 1810, 1811
- YTTRIUM**, 46; sepn. of erbium from, 1198; purification and at. wt. of. . . . . 2332
- Yttrium cobalticyanide. . . . . 1490
- ZINC**, revision of at. wt. of—electrolytic detn. of Zn in  $\text{ZnBr}_2$ . . . . . 868
- Zinc bromide, detn. of Zn in. . . . . 868
- Zinc salts, action of alkali on certain. . . . . 785
- Zingiberol. . . . . 430



PROCEEDINGS

OF THE

American Chemical Society

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FOR THE YEAR 1916

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# PROCEEDINGS.

## Contents.

### January.

General Society Minutes and Reports.....	1
Report of the Secretary of the American Chemical Society for the year 1915.	
Report of the Editor of the Journal of the American Chemical Society for the year 1915. Report of the Editor of Chemical Abstracts for the year 1915.	
Report of the Editor of the Journal of Industrial and Engineering Chemistry for the year 1915.	
Minutes of the Directors Meeting.....	8
Conucil.....	11
Members elected between November 15 and December 15, 1915.....	11
Meetings of the Sections:	
Lexington Section.....	15
The Effect of the European War on Drug Supplies, L. A. Brown. The Stability of Silver Fulminate under Water, A. M. Peter. The Translocation of the Mineral Constituents of Certain Seeds during Growth, G. D. Buckner. A Review of the Literature on the Distribution and Sources of Iodine in Plant and Animal Life, P. L. Blumenthal.	
Chicago Section.....	16
The Manufacture of Gasoline and Benzole from Petroleum and Other Hydrocarbons, Walter F. Rittman.	
Ames Section.....	16
Peculiarities of the Chemistry and Physics of Silicate Industries, Homer F. Staley.	
Maryland Section.....	16
Partition or Neutral Solubility, E. E. Reid and B. B. Wroth. Methods of Toxicological Examinations, W. B. D. Penniman.	
Louisiana Section.....	16
Some Aspects of Illuminating Gas Manufacture, C. Hartogh. Journal Reviews, Philip Asher. The Manufacture and Usages of White Lead, and The Crime of Carelessness (motion pictures).	
Wisconsin Section.....	16
The Influence of Impurities on the Rate of Growth of Ice Crystals, J. H. Walton, Jr. The Nature of Radiant Energy, R. A. Millikan.	
Cincinnati Section.....	17
University of Michigan Section.....	17
A Study of the Hydrochloric Acid Concentration Cell with Respect to Activity and Concentration, Boundary Potential and Transparent Members, A. L. Ferguson. Ferro-Tungsten as an Industry, R. L. Session.	
New York Section.....	17
University and Industry, Richard C. Maclaurin, Henry P. Talbot, William H. Walker, Arthur D. Little. The Naval Consulting Board of the United States, L. H. Baekeland and W. R. Whitney.	
Puget Sound Section.....	17
University of Illinois Section.....	17

# IV

Northeastern Section.....	17
The Chemistry of Amorphous Solids, Warren K. Lewis.	
Western New York Section.....	18
Electrons, Atoms, and Energy Quanta, Saul Dushman.	
California Section.....	18
The Equilibrium of Oxidation Reactions, Arthur A. Noyes. Hydrocarbon Reactions at High Temperature, Walter F. Rittman.	
Oregon Section.....	18
Some Modern Views of Matter, W. C. Morgan.	
Detroit Section.....	18
Formaldehyzed Capsules, Wilbur L. Scoville. Dental Surgery, Charles H. Oakman. A Piece of Cheese, John W. M. Bunker.	
Minnesota Section.....	18
The Nature of the Proteins Extracted from Wheat Flour by Various Processes, C. H. Bailey. Recent Advances in Chemotherapy, A. D. Hirschfelder. Flavoring Extracts and Baking Powders, Wm. Kennedy. The Polymerization of China Wood Oil, Carl Schuman. The Swelling of Rubber in Organic Liquids, I. H. Derby.	
Southern California Section.....	18
Carbon Tetrachlorid, L. H. Buck.	
New Haven Section.....	19
The Disposal of City Sewage, C. E.-A. Winslow and Anna M. R. Lauder.	
Rochester Section.....	19
American Resources in Fertilizer Materials, Frank K. Cameron.	
Washington Section.....	19
Some Examples of Metal Failures (illustrated), G. K. Burgess. Chemical Factors Affecting Electrolytic Corrosion in Soils and Reinforced Concrete, B. McCollom. The Action of Natural Waters on Boilers, R. B. Dole.	
Milwaukee Section.....	19
Development in the Marketing of Coal—Specifications, Storage, etc., S. W. Parr.	
Cleveland Section.....	19
The Electron Theory and Some of its Applications, A. G. Worthing.	
Nebraska Section.....	19
Our National Chemical Industries, Chancellor Samuel Avery.	
Columbus Section.....	19
The Life and Work of John Ulric Nef, W. L. Evans.	
Philadelphia Section.....	20
The Decomposition of Hydrocarbon Oils under High Temperatures and Pressures, and the Industrial Applications of the Process, Walter F. Rittman.	
Virginia Section.....	20
Some Mechanical Analogies in Electricity and Magnetism, W. S. Franklin.	
Pittsburgh Section.....	20
Demonstration of a Portable Gas Detector, G. A. Burrell. The Mechanism of Corrosion, James Aston. The Manufacture of Refractories, R. H. H. Pierce. Hydrometallurgy of Copper, Raymond F. Bacon. The Removal of Iron from a Municipal Water Supply, S. Buka.	
Connecticut Valley Section.....	20
Smoking Opium in the United States, H. L. Thompson. The Rittman Gasoline Process, E. C. Stone.	
Deceased Members.....	20

## February.

Council.....	21
Treasurer's Report.....	
Members elected between December 15, 1915 and January 15, 1916.....	25
Meetings of the Sections:	
Eastern New York Section.....	30
Garbage Reduction, W. W. Chadsey. Treatment of Sewage, W. E. Weller.	
Cincinnati Section.....	30
The Trend of American Technical Chemistry (illustrated), Thomas H. Norton. An Outline of Studies by the U. S. Public Health Service on the Pollution of the Ohio River (illustrated), W. H. Frost.	
Indiana Section.....	30
Commercial Applications of Oxygen, Philip J. Kroll.	
Washington Section.....	30
The Chemical Analysis of Animal Nutrition, C. L. Alsberg.	
Rochester Section.....	31
Thermal Reactions among Hydrocarbons in a Single Phase System, W. F. Rittman. Oils, F. R. Baxter. The Manufacture of Acids, M. H. Eisenhart.	
Connecticut Valley Section.....	31
Our Experience with Nickel Anodes, C. H. Corbin. Some Experiments in Making Electrolytic Copper Pipe, C. F. Wessell. Mechanical Plating and Polishing, G. B. Hoogaboom.	
Philadelphia Section.....	31
Pittsburgh Section.....	31
The Hydrometallurgy of Copper, Raymond F. Bacon. The Removal of Iron from a Municipal Water Supply, S. Buka.	
University of Missouri Section.....	32
Southern California Section.....	32
The Manufacture of the Illuminating Mantle, M. N. Lando.	
Ames Section.....	32
Compounds of Ammonia and Certain Metallic Salts, G. J. Fink. Is the Hydrochloric Acid of the Gastric Juice Efficient as a Germicide, C. C. Fowler.	
Columbus Section.....	32
Some Interesting Physical and Chemical Properties of Clay (illustrated), Arthur S. Watt. The Contributions of Chemistry to the Production and Preparation of Human Food, John F. Lyman. The American Chemist and the War Problem, James R. Withrow. The Fertilizer Resources of the United States, Frank K. Cameron.	
St. Louis Section.....	32
The Gasoline Situation in America, Walter F. Rittman. Some Relations between Chemical Constitution and Physiological Action, A. C. Bolyston. The Silver Coulometer, F. O. Anderegg.	
Virginia Section.....	33
Tannin, (paper read by Frank R. Elder).	
Nashville Section.....	33
The Simultaneous Developing and Fixing of Photographic Plates, James F. Norris.	
Cleveland Section.....	33
Experiment on the Electrolysis of Cyanide Solutions, M. F. Coobaugh.	
Lexington Section.....	33
Report on the Annual Convention of the Association of Official Agricultural	

## VI

Chemists, for 1915, Wm. Rodes, Jr. · Note on a Specimen of Ferric Phosphate from Laurel County, Kentucky, A. M. Peter. Chemical Changes Occurring during the Ripening of the Wild Goose Plum, J. S. McHargue.	
Wisconsin Section .....	33
Some Experiments on Animal Oxidations, A. S. Loevenhart.	
New York Section.....	33
Milwaukee Section .....	33
Kansas City Section.....	33
Deceased Members.....	33

## March.

Council .....	35
Members elected between January 15th and February 15th.....	37
Meetings of the Sections:	
California Section .....	40
Electrochemical Possibilities of California as Compared with those of Sweden and Norway, J. W. Beckman. Solutions of Metals in Liquid Ammonia, W. L. Argo.	
Northern Intermountain Section.....	40
Notes on the Homedale Nitrate and Potash Deposits, C. C. Todd. The Effect of Dihydroxystearic Acid and Uvitonic Acid in Soil and in Water Solution, P. P. Peterson. Gluten Formation in Wheat Kernel, George A. Olson.	
Lexington Section .....	40
Total Nitrogen as a Measure of the Organic Matter in Soils (Review), S. D. Averitt. Variation in the Mineral Composition of the Sap, Leaves and Stems of the Wild Grape Vine and the Sugar Maple Tree, O. M. Shedd.	
Indiana Section .....	41
Technical Application of Oxygen (illustrated), Philip J. Kroll. An Official View of Food Control Work, T. J. Bryan.	
Pittsburgh Section.....	41
Lubricating Greases: Their Composition and Methods of Analysis, Joseph E. Babb. Thermal Reactions among Hydrocarbons at High Temperatures, W. F. Rittman. The Corrosive Resistance of Copper Steel, D. M. Buck and J. O. Handy.	
Detroit Section .....	41
Formaldehyzed Capsules, Wilbur L. Scoville. The Theory and Practice of Case Hardening, Herman G. Kiefer.	
Virginia Section .....	41
Some Research Problems, J. B. Weems. Sulfides in Flowers of Sulfur, R. F. McCrackan, O. L. Barden and R. C. Courtney. Chemical Methods for Differentiating Cotton, Wool and Silk, E. C. L. Miller and J. C. Ford.	
New Haven Section.....	41
Oregon Section .....	42
Some Modern Views of Matter, Conger Morgan. The Synthesis of Metals, A. K. Knowlton.	
Georgia Section .....	42
Rhode Island Section.....	42
Green Gills in Oysters, P. H. Mitchell. Sympathetic on Induced Reactions, A. B. Lamb.	
Chicago Section.....	42
The Chemistry of Glass Making, Alexander Silverman.	



## VII

Philadelphia Section.....	42
The Extraction and Recovery of Radium and Vanadium from Carnotite, Charles L. Parsons.	
Minnesota Section.....	42
Animal Pigments, Ross A. Gortner. The Physiological and Biochemical Significance of Hydrogen Ion Concentration, J. F. McClendon. The Chemist and the Flour Industry, F. W. Emmons. Nonideal Solutions, E. K. Strachan.	
Puget Sound Section.....	42
Plasticity of Clays (illustrated), R. F. McMichael.	
University of Michigan Section.....	42
The Determination of Thorium in Monazite Sand, R. J. Carney.	
Cornell Section.....	43
The Electrolytic Production of Perchlorates, E. L. Mack. The Nitration Products of Phenoltetrachlorophthalein and Some of its Derivatives, J. J. Kennedy. The Electrolysis of Solutions of the Rare Earths, A. B. Ray.	
University of Illinois Section.....	43
Syntheses in the Naphthalene Series, H. B. McCluggage and Oliver Kamm. Triphenylmethyl, Laurence C. Johnson. Qualitative Tests for Drugs Con- taining Emodin, Ruth E. Okey and G. D. Beal. Preparation and Charac- terization of Trimethyleneoxide, C. G. Derick and D. W. Bissell. The Preparation of Conductivity Water, E. W. Washburn and H. J. Wieland.	
Kansas City Section.....	43
The Metallurgy of Vanadium, R. L. Grider. The Chemistry of Vanadium, P. V. Faragher. Vanadium Steels, Clarence Estes.	
Rochester Section.....	43
Sulfur, Alexander Smith.	
Wisconsin Section.....	43
A Neglected Principle of Chemistry, L. Kahlenberg.	
Connecticut Valley Section.....	43
The Chemistry of Synthetic Caoutchouc, Joseph S. Chamberlain. The Color Problem in the Paper Industry, R. F. Hatch.	
Maryland Section.....	43
The Estimation of Sugar in the Blood, Geo. Peirce.	
Cleveland Section.....	43
Radium and Radio-Activity, Chas. H. Viol.	
Columbus Section.....	43
Some Problems in Municipal Chemistry, C. B. Hoover. The Present Chemical Situation as Related to Problems in Water Purification, Charles P. Hoover.	
Western New York Section.....	44
Manufacture and Bacteriology of Ice Cream, H. F. Lichtenberg.	
Deceased Members.....	44
<b>April.</b>	
Council .....	47
Members elected between February 15 and March 15, 1916.....	49
Meetings of the Sections:	
Eastern New York Section.....	52
The Electrolytic Refining of Copper, F. D. Easterbrook.	
New York Section.....	52
Electrochemical War Supplies (read by title), Lawrence Addicks. Air Salt-	

# VIII

peter, W. S. Landis. Hydrogen for Military Purposes, E. D. Ardrey. New War Products, A. H. Hooker. Magnesium, W. M. Grosvenor. Liquid Chlorine, G. Ornstein. Electrolytic Zinc, W. R. Ingalls. The Acetyl Derivatives of the Sugars, C. S. Hudson. Development of the Bureau of Chemistry, Carl L. Alsberg.	
Milwaukee Section .....	53
The Uses of Wood Flour, Especially the Manufacture of Linoleum (illustrated), F. W. Kressmann.	
California Section .....	53
The Fundamental Principles Underlying Flotation, Joel H. Hildebrand.	
Eastern New York Section .....	53
The Great Telescopes of the World and the Discoveries Made by Their Use, John A. Brashear. Ultra-Violet Light, R. D. Kleeman. The Electrolytic Refining of Copper, F. D. Easterbrook.	
University of Missouri Section .....	53
Some Aspects of Fat Metabolism, New Physiological, C. W. Greene.	
Kansas City Section .....	53
The Fate of Food Protein in the Animal Body, P. A. Shaffer. High Alloy Steels for Long Span Bridges, J. A. L. Waddell. A Picric-Phosphotungstic Acid Clarifier for Sugar in Meat Extracts, W. B. Smith. Flotation, George Belchic. Heat Value of Gas of the Mid-Continental Field, H. C. Allen.	
Chicago Section .....	54
The Present Status of Fertilizer Theory and Practice, W. D. Richardson. The Chemistry and Metabolism of the Nucleic Acids, H. Gideon Wells.	
Cincinnati Section .....	54
The Application of Physical Chemistry to Some Geological Problems, Otto Charles von Schlichten. Various Aspects of the Smoke Problem, Osborn Monnett.	
Puget Sound Section .....	54
The Electrical Fixation of Nitrogen, J. D. Roso. Fisheries Products, Geo. H. Stillman. Potash from Kelp, I. F. Laucks and H. Mahschmedt. Potash from Mineral Resources, G. A. Newhall. Phosphate Rocks, G. E. Weaver.	
Nashville Section .....	54
The Utilization of Waste in the Manufacture of Copper, J. T. McGill. Estimation of Extract of Beef, E. A. Ruddiman.	
Nebraska Section .....	54
The Laboratory Examination of Clays, George Borrowman.	
Louisiana Section .....	54
The Oxidation of Ethyl Alcohol by Means of Potassium Permanganate (No. 2), Jesse E. Day. The Syrup Precipitate in the Direct Manufacture of White Cane Sugar, C. E. Coates and L. C. Slater. Some Notes on the Chemical Control of Petroleum Refineries, C. E. Coates and M. M. Merritt.	
Rochester Section .....	54
Sewage Disposal, C. C. Hopkins. The Photographic Microscope in Analysis, Fred Wright.	
Ames Section .....	55
The Evolution of the Elements and the Periodic System, William D. Harkins.	
Washington Section .....	55
The Action of Light on Chlorine with Special Reference to the Formation of Chloroacetic Acid, H. H. Curtis. The Isolation of Vitamines from Brewer's Yeast, A. Seidell. On the Chemical Nature of Vitamines, R. R. Williams.	

St. Louis Section .....	55
Activated Sludge, Edward Bartow.	
Cleveland Section .....	55
Glass, Alexander Silverman. The Heat Temperature of Steel, R. R. Abbott.	
Virginia Section .....	55
The Revolution in Coke Manufacture and its Relation to Our National Welfare, Charles H. Herty.	
University of Michigan Section .....	56
Glass Defects, E. C. Sullivan.	
Connecticut Section .....	55
Electrical Precipitation of Flue Dust, Mr. Egbert. Manufacture and Testing of Cold Rolled Steel, F. W. Shaefer.	
Philadelphia Section .....	55
Modern Painting Practices on Structural Material, George B. Heckel. The Chemistry of Glass Making, Alexander Silverman.	
Detroit Section .....	56
The Chemical Composition of Steel in Relation to its Industrial Uses, Jos. N. Bourg.	
Western New York Section .....	56
Manufacture of Ice Cream, Harry F. Lichtenberg. The Chemistry of Photography, F. C. Frary.	
Oregon Section .....	56
The Synthesis of Metals, A. A. Knowlton.	
New Haven Section .....	56
On the Synthesis of Pyrimidine—Rosaniline Dyes, T. B. Johnson. On the Metallic Gallium and Some Gallium Reactions, P. E. Browning. The Effect of Freezing Precipitated Inorganic Colloids, Blair Saxton. An Apparatus for Determining Freezing-Point Lowering, R. G. Van Name and F. G. Brown.	
Maryland Section .....	56
By-Product Coke Oven Operation, B. W. Winship.	
Wisconsin Section .....	56
The Electron Theory, M. Mason.	
Lexington Section .....	56
Investigations on the Abderhalden Test for Pregnancy, W. S. Anderson. The Duties of the United States Assay Commission, F. E. Tuttle. Some Queer Colloidal Precipitations, C. A. Nash.	
Maine Section .....	56
Control of Sulfite Digestion by Titration Methods, A. G. Durgin. The Purchase Heat, A. B. Andrews. The Pulp and Paper Industry, R. H. McKee.	
Deceased Members .....	56

## May.

Council .....	57
Members elected between March 15 and April 15, 1916 .....	57
Meetings of the Sections:	
Chicago Section .....	61
Practical Vapor Pressures and Distillation, M. A. Rosanoff.	
Lexington Section .....	61
Note on the Occurrence of Gallium, R. N. Maxson. A Recent Discovery with Reference to the Bang Bacillus, E. S. Good. The Separation and Estimation of Polysulfids and Thiosulfate in Lime-Sulfur Solution, S. D. Averitt.	

Washington Section.....	61
A Practical Demonstration of Some of the Principles of Colloidal Chemistry, John Uri Lloyd.	
Minnesota Section.....	62
The Factors Influencing the Occurrence of HCN in Plants, J. J. Willaman. The Reimer-Tiemann Reaction, W. H. Hunter.	
Southern California Section.....	62
The Bunsen Flame in Old and New Light, Wilhelm Hirschkind.	
Rhode Island Section.....	62
The Bacterial Treatment of Textile Fibers, F. P. Gorham.	
University of Illinois Section.....	62
The Raw Material of Varnish, C. T. Bragg.	
Louisiana Section.....	62
On the Determination of Diastatic Power in Wheat Flour, M. A. Schneller. The Influence of Phosphates on Alcoholic Fermentation, Wm. L. Owen. Dis- cussion of the By-Products of Rice Milling, F. W. Liepsner.	
Puget Sound Section.....	62
Opportunities for Electrochemical Industries, C. E. Bogardus. Bleaching Powder Costs, Hainsworth. Artificial Abrasives, J. Daniels. The Produc- tion of Alkalies and Salts from Sea Water, H. L. Trumbull.	
South Carolina Section.....	62
Abstract, Report of Referee Nitrogen Determination, R. N. Brackett. Calomel Standard Cell, and the Various Thermodynamic and Thermochem- ical Relations Occurring in the Cell, C. F. Lipscomb. Gravitation, J. E. Mills. A Note upon Methods for Determining Acidity in Soils, C. J. King. The Relation of the State Laboratories to the Commercial Chemist, Boyden Nims.	
University of Missouri Section.....	63
The Methods of Radium Extraction from Carnotite Ore Used by the Na- tional Institute at Denver, Colo., Herman Schlundt.	
Oregon Section.....	63
Sulfur and Soil Acidity, Two Important Factors in the Fertility of Soils, H. V. Tartar.	
Connecticut Valley Section.....	63
Manufacture of Celluloid, Herbert E. Nims. Some Analyses of Rocks from the Islands of the Pacific, E. W. Morley. Browning of Gun Barrels, C. F. Wessell.	
University of Michigan Section.....	63
Negative Osmose, F. E. Bartell.	
Maryland Section.....	63
Coal Gas Residuals (illustrated), Frederick H. Wagner.	
Cleveland Section.....	63
The Microscope and Its Accessories, L. B. Hall.	
Cincinnati Section.....	63
The History, Characteristics and Methods of Manufacture of Modern Explosives, M. F. Lindsley.	
Iowa Section.....	63
A Plant for the Manufacture of Synthetic Phenol, Harry McCormack.	
Virginia Section.....	63
Some Chemical Classics, Garnett Ryland. Some Phenomena of Lightning and Lightning Prevention, R. E. Loving. The Relation of Research to Everyday Life, J. B. Weens.	

Rochester Section.....	64
The Character, Cost and Adulteration of Foods, A. P. Sy. Velocity of Heterogeneous Reaction with Especial Reference to Catalysis, Irving Langmuir. The Organization of Industrial Research, C. E. Kenneth Mees.	
Syracuse Section.....	64
Some Problems in Agricultural Chemistry, G. W. Cavanaugh. The Decennial of Electric Steel in America, G. M. Berry.	
Pittsburgh Section.....	64
Thermal Reactions among Hydrocarbons at High Temperatures, W. F. Rittman. The Corrosion Resistance of Copper Steel, D. M. Buck and J. O. Handy.	
Joseph Priestly, F. C. Phillips. The Extraction of Radium from its Ores, Charles Parsons.	
California Section.....	64
Some General System of Acids and Bases, Merle Randall.	
Deceased Members.....	64

## June.

General Meeting.....	65
Directors' Meeting.....	68
Council.....	69
Minutes of the Council Meeting.....	69
Report of the Committee on the Western Campaign and Mr. Lewis B. Allyn's Connection Therewith.....	72
Members elected between April 15 and May 15, 1916.....	80
Meetings of the Sections:	
Alabama Section.....	82
The Role of the Chemist in the Cement Industry, Clarence N. Wiley. Isotopic Elements, Stewart J. Lloyd.	
South Dakota Section.....	82
The Free Energy of Dilution of Sulfuric Acid, Orville E. Cushman and Merle Randall. A Study of Canned Salmon (a preliminary note), Cecil Clemens and Sylvanna Elliott. A Modified Scheme for Qualitative Analysis, O. R. Overman. The Nitro Phenyl Ethers, Hilton Ira Jones and Alfred N. Cook. Some Subjects under Investigation in the Chemical Laboratories of the University of South Dakota, Alfred N. Cook.	
Milwaukee Section.....	83
Metallography of Iron and Steel (illustrated), C. J. Atkinson. Through the Furnace to the Farm, H. E. Horton.	
Northern Intermountain Section.....	83
Two Methods for the Separation of the Alkaline Earth Group, Alice G. Paterson. Recent Advances in Ore-Dressing, R. R. Goodrich. Composition and Baking Value of Dry Farmed and Irrigated Wheat, J. S. Jones. Electric Laboratory Heating Device, Harry Redekey Rupert.	
Indiana Section.....	83
Chemistry as an Aid to the Efficiency of Democracy, Chas. H. Herty. Detection of Nickel and Cobalt Salts, A. R. Middleton. Nonprotein Forms of Nitrogen in Alfalfa, R. H. Carr. Electromotive-Force Measurements with Tenth Normal Hydrochloric Acid and Calomel Electrodes, N. E. Loomis.	

Columbus Section.....	83
Rate of Absorption of $\text{CO}_2$ by Soda-lime, C. W. Foulk. Determination of Transition Points by Difference of Potential Methods, I. M. Geiger.	
California Section.....	84
Borax and its Uses, T. M. Cramer. The Chemistry of Copper Ore Enrichment, S. W. Young. Methods by which the Civilian Engineers Can Prepare Themselves to Assist the Engineer Corps of the U. S. Army in Case of War, Richard Park. The Work at the Military Training Camps, John Murphy. An Outline of the Work of the Organization for Industrial Preparedness of the Naval Consulting Board, A. H. Babcock.	
Pittsburgh Section.....	84
Constitution of Porcelains, A. A. Klein.	
St. Louis Section.....	84
Modern Methods in the Manufacture of Steel Castings, W. C. Hamilton. The Biological Chemistry of the Colon Group, Frederick A. Baldwin.	
North Carolina Section.....	84
The Action of Ammonia on Arsenic Iodide, Chas. H. Herty and C. B. Carter. Some Properties of the Solutions of Substantive Cotton Dyes, F. E. Carruth. Electrolysis of Certain Inorganic Salts in Liquid Ammonia Solution, C. F. Miller. The Chemistry of Gossypol, W. A. Withers and F. E. Carruth.	
Iowa Section.....	85
Electromotive Forces and Electrode Potentials in Pure and Mixed Solvents, II, F. S. Mortimore and J. N. Pearce. Barium in Tobacco, Nicholas Knight. Pure Sodium Chloride, Nicholas Knight. Acid Potassium and Sodium Phthalates as Standards in Acidimetry and Alkalimetry (Second Paper), W. S. Hendrixson. Auxamylases, E. W. Rockwood. Conditions Existing in Solutions near the Critical Temperature (a preliminary paper), P. A. Bond. A Comparison of Barbituric Acid, Thiobarbituric Acid and Malonylguanidine as Qualitative Precipitants for Furfural, A. W. Dox and G. P. Plaisance. An Aeration Method for Determining Alcohol in Fermentation Mixtures, A. W. Dox and A. R. Lamb. Relative Influence of Bacteria and Enzymes on Silage Fermentation (preliminary report), A. R. Lamb. Estimation of Calcium in Ash of Forage Plants and Animal Carcasses, S. B. Kuzirian.	
Wisconsin Section.....	85
Some Characteristics of Base Metal Thermocouples, O. L. Kowalke. The Theory of Distillation, M. A. Rosanoff.	
Rochester Section.....	85
The Development of Calorimetry, W. R. White. The Mercurial Thermometer and its Adaption to Industrial Arts, H. Y. Norwood.	
Louisiana Section.....	85
A Preliminary Report on Raw Materials Available for Certain Louisiana Chemical Industries, by the Committee on Resources, Chas. E. Coates.	
University of Michigan Section.....	86
Some Relationships between Ionization and Structure in Unsaturated Acids, Oliver Kamm.	
New Haven Section.....	86
The Experimental Methods of the Badische Anilin and Soda Fabrik, B. C. Hesse.	
Detroit Section.....	86

The Rare Gases, H. P. Talbot. Modern Facts on Cider Vinegar, Floyd W. Robison.	
Syracuse Section.....	86
The Flow of Heat through Furnace Walls. Radiation of Heat from Furnaces. Proper Materials to be Used in the Making of Mortar for Use in Furnaces, J. W. Richard.	
Chicago Section.....	86
New York Section.....	86
University and Industry, William H. Nichols.	
Eastern New York Section.....	86
The Mendelian Theory of Heredity and the Determination of Sex (illustrated), H. B. Goodrich. Calorimetry: The Development of Calorimetry, W. P. White.	
Western New York Section.....	87
Hydrofluoric Acid and Fluorides, K. F. Stahl. The Common Refractory Oxides, Robert B. Sosman.	
Philadelphia Section.....	87
The Manufacture of Vaccines and Serums, C. W. Brown.	
Lexington Section.....	87
Note on the Occurrence of Gallium, R. N. Maxson. The Growth of Isolated Plant Embryos, G. D. Buckner. On the Reaction between Iodine and Tetrathionate, P. L. Blumenthal.	
Cleveland Section.....	87
The Relations in Origin and Composition of Coal, Petroleum and the Natural Asphalts, C. F. Mabery.	
Washington Section.....	87
The Preparation of Heavy Metal Salts of Certain Organic Acids, C. N. Myers. Some Observations upon the Toxicity and Chemotherapy of the Heavy Metals, G. C. Lake. The Separation and Determination of Small Amounts of Antimony, Elias Elvove.	
Oregon Section.....	87
The Synthesis of Metals, A. A. Knowlton.	
Maryland Section.....	88
Measurement of Osmotic Pressure of Concentrated Sugar Solutions, R. T. Myrick. Esterification of Acids by Mercaptans, J. H. Sachs and J. W. Kimball. Catalytic Preparation of Nitriles, G. D. Van Epps. The Identification of Acids, J. A. Lyman and E. Emmet Reid. The Manufacture of Ethyl Alcohol, H. W. Berger.	
Deceased Members.....	88

## July.

Council.....	89
Members elected between May 15 and June 15, 1916.....	89
Meetings of the Sections:	
Indiana Section.....	90
Theory and Practice of Making Serums and Vaccines, Severance Burrage.	
St. Louis Section.....	90
The Determination of Water and Alcohol in Ether, Edward Mallinckrodt, Jr.	
Kansas Section.....	90
Ancient Chemistry (illustrated), F. B. Dains. The Chemical Conditions	

Necessary for Making Alfalfa Silage, C. O. Swanson. Notes on New and Non-official Remedies and the Propaganda of Reform, R. H. Needham. On the Nutritional Deficiencies of Corn, J. T. Willard.	
Eastern New York Section.....	91
Manufacture and Uses of Linseed Products, A. C. Goetz. The Dye Situation, Aug. Amrein.	
New York Section.....	91
Some Problems in the Petroleum Industry, Raymond F. Baker. An Account of Some Experiments Relating to Vapor Pressures, Fractional Distillation, Critical Data and Compressibility of Gases, George A. Burrell. The Petrographic Microscope in Analysis, Frederick E. Wright.	
Nashville Section.....	91
Studies in Preservation of Diphtherial Toxin, for Schlick's Test, Wm. Litterer.	
Washington Section.....	91
The Machine Shop and the Chemical Laboratory as Related to National Preparedness for Defense, Joseph Steinmetz.	
Cincinnati Section.....	91
Milk Clarifiers, Clarence Bahlmann.	
University of Michigan Section.....	91
The Molecular Weights of Free Radicals, C. S. Schoepfle.	
Nebraska Section.....	92
Some Substances Essential to Growth, John W. Calvin. Life and Work of Professor J. U. Neff, F. W. Upson.	
Pittsburgh Section.....	92
Smelter Smoke and Arsenical Poisoning, W. D. Harkins. Chemistry and the Present War: How it May Affect the Future of the Chemical Industries in the United States, L. H. Baekeland.	
Louisiana Section.....	92
The Estimation of Minute Qualities of Sulfur Dioxide in the Atmosphere, C. S. Williamson, Jr. Notes on the Analysis of Aspirin, C. L. Clay.	
Cornell Section.....	92
Some Topics in Luminescence, E. L. Nichols.	
Cleveland Section.....	92
Water Powers of the United States, Herman Stabler. Acid Resisting Alloys, W. C. Carnell.	
Rochester Section.....	92
Chicago Section.....	92
Our Responsibilities, B. C. Hesse.	
Vermont Section.....	92
Detroit Section.....	93
New Haven Section.....	93
Some Recent Developments in Glasses and the Art of Glass Blowing, Charles A. Kraus.	
University of Illinois Section.....	93
A Theory of the Formation of Smooth Deposits by Electrolysis, A. MacInnes and Morgan. The Contamination of Precipitates, G. McP. Smith.	
Syracuse Section.....	93
Some Phases of Glass Manufacture, E. C. Sullivan.	
Puget Sound Section.....	93
Products of the Lumber Industry, Dr. Benson.	
Van't Hoff Fund.....	93



Deceased Member (Harry Clay Jones).....	94
-----------------------------------------	----

## August.

Council.....	97
Members elected between June 15 and July 15, 1916.....	97
Meetings of the Sections:	
Western New York Section.....	98
Puget Sound Section.....	98
The Resources and Industries of the Philippines, Horace G. Deming.	

## September.

Council.....	99
Members elected between July 15 and August 15, 1916.....	99
Deceased Members.....	100

## October.

Council.....	101
Members elected between August 15 and September 15, 1916.....	101
Meetings of the Sections:	
Chicago Section.....	102
The Manufacture of Synthetic Phenol, Harry McCormack. Synthetic Phenol Resins for Printing Plates—A Special Application of Anhydrous Resins, L. V. Redman, A. J. Weith and F. P. Brock.	
Rochester Section.....	102
Deceased Members.....	102

## November.

General Meeting.....	103
Directors' Meeting Minutes.....	107
Council.....	109
Council Minutes, New York Meeting.....	109
Majority Report of the Committee on Professional Ethics.....	110
Minority Report.....	112
The Future of the Industrial Journal.....	113
The Remedy.....	115
Members elected between September 15 and October 15, 1916.....	119
Meetings of the Sections:	
California Section.....	122
Colloids and Biology, Martin H. Fisher. The Use of Petroleum in Smelting Iron Ore, A. E. Bourcond.	
Chicago Section.....	122
The Evolution of the Elements and Structure of Atoms, W. D. Harkins.	
Cincinnati Section.....	122
Exfoliation and Carbon Concentration in the Case-Hardening of Steel, Edwin P. Stenger.	
Cleveland Section.....	122
Some Recent Researches in Colloid Chemistry, Harry N. Holmes.	
Connecticut Valley Section.....	122
Coöperation between the College and Industry, M. L. Crossley.	

## XVI

Detroit Section.....	122
Agricultural Chemistry: Its Present Status in the United States, and its Relation to the National Food Problem, H. J. Wheeler.	
Eastern New York Section.....	123
Geology and Geochemistry of the Saratoga Quadrangle, J. H. Stoller.	
Indiana Section.....	123
Chemical Science in Indiana, R. H. Ransom.	
Lexington Section.....	123
The Chemistry of Bread-Baking, R. C. Dabney.	
Maryland Section.....	123
The Hydrolysis of Ethyl Sulfuric Acid, W. W. Randall.	
New York Section.....	123
Why Our Chemical Import Statistics Should be Overhauled, Bernhard C. Hesse.	
Philadelphia Section.....	123
Early History of Chemical Industry in Philadelphia, Samuel P. Sadtler.	
Pittsburgh Section.....	123
(a) Revision of Our Chemical Import Statistics; (b) Ten-Year Index to Chemical Abstracts, W. C. Cope. The Properties of Some European Bonding Clays, A. V. Bleining. The Viscosity of Blast Furnace Slags, A. L. Field. The Extraction of Cerium and Preparation of its Salts, C. T. Vogt.	
Puget Sound Section.....	124
The Genesis of the Elements, W. D. Harkins.	
Rhode Island Section.....	124
Made in America Porcelain, C. F. Quaintance. Denver Fire Clay Products, W. W. Case.	
Rochester Section.....	124
Photo-Engraving, A. J. Newman. The Teaching of Elementary Chemistry, H. A. Carpenter.	
St. Louis Section.....	124
The New United States Pharmacopoeia, C. E. Caspari.	
Syracuse Section.....	124
University of Illinois Section.....	124
Chemical Literature and its Use, Marian E. Sparks.	
Wisconsin Section.....	124
The Constitution of Steel, Bradley Stoughton.	

## December.

Council.....	125
Members elected between October 15 and November 15, 1916.....	125
Meetings of the Sections:	
Alabama Section.....	127
Some Interesting Data on the Decomposition of Ammonia by Heat, Julius K. Munster.	
Ames Section.....	128
California Section.....	128
The Outlook for Cheap Oxygen, F. G. Cottrell. Modern Views of Metallic Conditions, G. E. Gibson.	
Chicago Section.....	128
Notes on the Secretion and the Chemistry of the Human Gastric Juices, A. J. Carlson.	

# XVII

Cincinnati Section.....	128
Methods of Isolation and Identification of <i>B. coli</i> Now Used at the Cincinnati Filtration Plant, S. J. Hauser. Relation of Microorganisms to the Loss in Head in Rapid Sand Filters, J. W. Ellms and S. J. Hauser.	
Columbus Section.....	128
The Electrolytic Production of Antimony, D. J. Demorest.	
Connecticut Valley Section.....	128
Some Effects of Impurities in Boiler Feed Water, C. S. Williams. The Production of Aromatics from Petroleum, E. C. Stone.	
Detroit Section.....	128
Synthetic Resins, Leo H. Baekeland.	
Eastern New York Section.....	129
Recent Methods in the Study of Proteins, P. A. Kober. Remissions in Leukemia Produced by Radium in Cases Completely Resistant to X-Ray and Benzol: (a) Clinical Study, Thomas Ordway; (b) Metabolism Study, Arthur Knudson and Theodore Erdos. Recent Development in the Bio-Chemical Study of Lipins, Arthur Knudson	
Indiana Section.....	129
Researches on Local Anaesthetics, A. B. Davis. Use of the Hydrogen Electrode in Bacteriology and Soil Chemistry, E. Edward Loomis.	
Louisiana Section.....	129
Some of the Applications of Colloidal Chemistry to the Industry, C. T. Dowell.	
Maryland Section.....	129
The Hydrolysis of Ethyl Sulfuric Acid, W. W. Randall.	
Minnesota Section.....	129
Estimation of Hydrocyanic Acid and the Probable Form in Which it Occurs in Sorghum, J. J. Willaman.	
Nashville Section.....	129
Conductivity Measurements of Precipitation Reactions, E. L. Carter.	
New York Section.....	130
The General Problem of Public Service Training, Chas. A. Beard. The Status and Compensation of the Chemist in Public Service, Frederick E. Breithut. The Chemist in the Service of New York City, Otto H. Klein. The Chemist in Public Service, Harvey W. Wiley.	
Philadelphia Section.....	130
The Mechanics of Astronomy, John A. Miller	
Rochester Section.....	130
The German Alarm Clock, H. E. Horne.	
St. Louis Section.....	130
Methods and Effects of Wood Preservation, Hermann von Schrenk.	
Wisconsin Section.....	130
The Use of Bark for Paper Specialties, Otto Kress.	
University of Missouri Section.....	130
Advances in Science; the Offspring of Radioactivity, Herman Schlundt. The Influence of Pressure on Solubilities, H. F. Sill.	
Deceased Members.....	130



# Proceedings.

## GENERAL SOCIETY MINUTES AND REPORTS.

On November 1st, a nominating ballot was sent to all members of the Society as required by the Constitution, the following being the nominees of the membership sent to the Council for election:

For President: C. H. Herty, Julius Stieglitz, Louis Kahlenberg and L. H. Baekeland.

For Councilors-at-Large: W. D. Bigelow G. N. Lewis, F. N. Smalley, Geo. D. Rosengarten, Edward Bartow, L. W. Jones, Wm. Brady, B. C. Hesse.

The ballot was counted by a committee consisting of C. L. Parsons, J. A. LeClerc, and John Johnston, assisted by seven other members of the Society.

The result of the election by the Council will be found in the Council minutes.

### Report of the Secretary of the American Chemical Society for the Year 1915.

The growth of the American Chemical Society during the year 1915 was greatly affected by the foreign war. However, our membership has increased over that of 1914. The Society has made a net gain of 247 members during the year. The membership of the Society at the end of 1914 was 7170. It is now 7417. Statistics follow:

Honorary members	15
Life members.	13
Corporation members	57
Members	7,332
Total	7,417

During the year the deaths of the following members were reported to the Secretary: R. E. Berger, Cleveland, Ohio; R. K. Birley, East Orange, N. J.; John M. Davison, Santa Barbara, Calif.; Dr. F. Eckhardt, Grasselli, N. J.; J. S. Wm Greth, Pittsburgh, Pa.; Chas. M. Hall, Niagara Falls, N. Y.; S. H. Hartig, Pittsburgh, Pa.; John K. Hamilton, Pittsburgh, Pa.; J. Langeloth, N. Y. City; D. W. Lewis, Cleveland, O.; Robt. L. Maury, Saranac Lake, N. Y.; N. Frederick Merrill, Burlington, Vermont; Gail Mersereau, Brooklyn, N. Y.; Hugh Allan Murta, Man., Canada; H. H. McGregor, Cleveland, Ohio; J. U. Nef, Chicago, Ill.; J. H. Pettit, Urbana, Ill.; Albert Plaut, N. Y. City; Howard E. Reid, Siegfried, Pa.; J. Roemer, White Plains, N. Y.; Elwood D. Rood, Enid, Oklahoma; David Stern, Cincinnati, Ohio; W. M. Stiles, Long Island

City, N. Y.; Richard Sommer, Milwaukee, Wis.; F. W. Spanutius, Hastings-on-Hudson, N. Y.; T. B. Stillman, Jersey City, N. J.; Wirt Tassin, Washington, D. C.; Henry L. Wheeler, Hartford, Conn.; Chas. N. White, Wilmington, Del.; James G. Woolworth, Providence, R. I.; C. W. Wright, Rock Island, Ill.

The number of members not in arrears registered in the Local Sections on November 30, 1914, was 5,414; the number on November 30, 1915, was 5,527. The number in each Section for 1914 and 1915 is noted below:

Local section.	Number of paid mem- bers, 1914.	Number of paid mem- bers, 1915.	Cash retained from balance, 1914.	Total Dr. account, 1915.
Alabama.....	33	27	4.97	29.97
Ames.....	...	32	...	11.62
California.....	179	183	...	150.00
Chicago.....	486	502	...	365.25
Cincinnati.....	115	118	...	143.75
Cleveland.....	166	170	...	160.00
Columbus.....	69	65	2.98	86.25
Connecticut Valley.....	68	67	...	75.00
Cornell.....	42	36	20.60	63.00
Detroit.....	71	68	1.58	88.75
Eastern New York.....	58	59	7.65	7.65
Georgia.....	57	59	...	71.25
Indiana.....	101	99	9.27	126.25
Iowa.....	54	39	41.35	66.35
Kansas City.....	80	95	0.55	100.00
Lehigh Valley.....	64	65	20.72	70.72
Lexington.....	21	19	10.34	10.34
Louisiana.....	31	42	8.25	67.50
Louisville.....	15	7	...	...
Maine.....	47	45	9.90	34.90
Maryland.....	78	84	...	97.50
Milwaukee.....	63	65	...	75.00
Minnesota.....	82	80	34.49	84.49
Nashville.....	21	23	12.67	12.67
Nebraska.....	27	28	34.20	50.00
New Haven.....	57	54	36.79	61.79
New York.....	1,057	1,076	38.30	538.30
North Carolina.....	36	27	0.10	50.10
Northeastern.....	507	436	38.67	288.67
Northern-Intermountain.....	20	19	...	...
Oregon.....	28	28	2.31	50.00
Philadelphia.....	307	358	39.36	214.36
Pittsburgh.....	258	259	...	190.00
Puget Sound.....	44	54	5.60	67.50
Rhode Island.....	65	64	20.22	45.22
Rochester.....	31	33	...	50.00
St. Louis.....	91	91	...	75.00
Southern California.....	97	114	12.04	112.04
South Carolina.....	25	26	11.85	36.85

Local section.	Number of paid mem- bers, 1914.	Number of paid mem- bers, 1915.	Cash retained from balance, 1914.	Total Dr. account, 1915.
Syracuse.....	95	96	30.95	118.75
University of Illinois.....	109	124	16.59	116.59
University of Michigan.....	38	37	20.07	20.07
University of Missouri.....	15	20	16.06	41.06
Virginia.....	...	59	...	25.00
Washington, D. C.....	327	285	..	245.25
Western New York.....	104	109	19.30	50.00
Wisconsin.....	86	81	16.75	66.75
	5,419	5,527	\$544.48	\$4,511.51

The table gives a summary of the sectional accounts for the year, shows the number of members in each Section for the present year and during 1914, the funds held over from 1914 account, and the total funds (which include the balances) charged to the 1915 account.

During the past two fiscal years, December 1, 1913, to November 30, 1915, the Secretary has made collections to the amount of \$76,805.97 in 1914 and \$80,189.22 in 1915, as follows:

	1914.	1915.
Membership dues.....	\$65,953.00	\$67,846.00
Subscriptions.....	5,761.59	6,676.32
Back numbers.....	2,514.07	2,548.63
Postage.....	1,054.13	1,084.07
Reprints.....	930.10	1,541.57
Exchange.....	19.44	17.36
Interest.....	373.64	475.27
Life membership.....	200.00	...
	<hr/> \$76,805.97	<hr/> \$80,189.22

These amounts were duly transmitted to the Treasurer of the Society.

Subscription and the sale of back numbers during the past year have again increased.

Several complete sets of our Journal have been sold to foreign and domestic libraries and several incomplete sets have been completed by the purchase of odd volumes where they could not be furnished from stock. The stock has been kept in good condition by the purchase of numbers needed to complete full volumes and by reprinting two small numbers issued in the early years of the Society. A few complete sets are still available for sale.

Back numbers are mailed direct from Easton, Pennsylvania, on orders sent out through the Secretary's Office. The following is a summary of the back numbers sent out by the Secretary during the year, together with the present stock of Journals and the condition of the Society's mailing lists:

Copies of the Society's publications sent out from December 1, 1914, to November 30, 1915, aside from mailing lists.....		28,721
Copies of the <i>Jour. Amer. Chem. Soc.</i> in stock.....		27,849
Copies of the <i>Chemical Abstracts</i> in stock.....		27,200
Copies of the <i>Jour. Ind. &amp; Eng. Chem.</i> in stock.....		8,976
Copies of the General Index, Vols. 1-20, <i>J. A. C. S.</i> in stock....		444
Copies of the Anniversary Number in stock.....		276
Mailing list for both Journals and <i>Chemical Abstracts</i> .....		6,779
Mailing list for <i>Chemical Abstracts</i> only.....		245
Mailing list for <i>Jour. Amer. Chem. Soc.</i> only.....		487
Mailing list for <i>Jour. Ind. &amp; Eng. Chem.</i> only.....		550

The Secretary wishes again to express to the members of the Society his appreciation for their continued assistance and loyal support of his efforts to administer the duties of his office. Without this aid little could have been accomplished. Respectfully submitted,

CHARLES L. PARSONS, *Secretary.*

### Report of the Editor of the Journal of the American Chemical Society for the Year 1915.

During the past three years papers and book reviews have been published as follows:

	Pages.			Number of papers.		
	1913.	1914.	1915.	1913.	1914.	1915.
Proceedings.....	114	112	96	...	...	...
Physical and Inorganic.....	1029	1154	1512	107	115	169
Organic and Biological.....	918	1320	1233	111	136	147
Book Reviews.....	75	80	43	85	83	52

Six papers have been referred to the Editor of the *Journal of Industrial and Engineering Chemistry* as more suitable for publication in that Journal than in the JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, forty-two papers have been returned to the authors for revision, or because they were not considered suitable for publication, thirty-nine papers have been published after revision made at the suggestion of the Board of Editors.

The increase in the numbers of papers published has been greater than the increase of the previous year, but the increase in the number of pages has been considerably less. This is because the Board of Editors have found it necessary to insist upon a concise form for papers which are to be published.

The circulation of the JOURNAL for December, 1915, was 7270 copies. With the exception of our own *Journal of Industrial and Engineering Chemistry* we know of no other journal in the world, publishing original articles in chemistry, that has a circulation over 5000 and, so far as we are informed, no other journal which publishes such articles in America has one-tenth of the circulation of our journals. In the light of these facts it is evident that our journals furnish the only means by which an



author can reach any large proportion of the chemists of the country. It has always been our policy to publish all suitable articles which are submitted to us. The relation which our journals has to the chemists of the country lays upon us a strong obligation to do this.

It is evident that we can continue this policy, however, only by the most careful scrutiny of all papers with a view to possible abbreviation. We wish to urge authors, most earnestly, to keep this in mind in preparing their papers. Unless it is necessary for the purpose of securing priority, no paper should be published until the experimental work of which it treats is brought as nearly as possible to a satisfactory conclusion. We cannot well afford space for half-finished or inaccurate work. Historical references should be very brief and should consist largely of references to the literature. All tables should be put into a form which will occupy the least possible space in printing. Authors should also consider carefully just how much of their original data is really essential for the information of future workers in the same field. In many cases averages are better than the complete data, and constants which result from a series of observations may be given without complete data, if they are accompanied by a careful statement of the degree of concordance which has been obtained.

In many cases members of our Board of Editors, who, it will be remembered, serve without any compensation, spend a good deal of time in preparing careful, detailed criticisms of papers with a view to their improvement before publication. We wish here to express our appreciation of the kindly way in which most authors receive these criticisms. As one member of the Board has put it, "we would much rather accept a paper than to reject it, and we would also much rather publish a paper as it is received than insist on its abbreviation or revision."

WILLIAM A. NOYES, *Editor*.

### Report of the Editor of Chemical Abstracts for the Year 1915.

As was to be expected, the war in Europe has had a marked effect on *Chemical Abstracts* during the past year. Although the field has been covered as completely as in normal times, the number of abstracts published during 1915 (18,449) is only 75.8% of the average for the three preceding years (24,339), when claim was properly made that the journal closely approached completeness. In some cases delays in the appearance of abstracts have been necessary, due to difficulties in obtaining journals from the countries involved in the war.

The average length of the abstracts in the 1915 volume, as compared with those of previous years, is shown in the following table:

Year.		1907.	1908.	1909.	1910.	1911.	1912.	1913.	1914.	1915.
Page	Journal article ab-									
	stracts.....	0.324	0.270	0.224	0.223	0.205	0.183	0.173	0.180	0.207
	Patent abstracts..	not detd.		0.096	0.103	0.108	0.077	0.083	0.084	0.093

The need of fuller abstracts in many cases has long been felt; with the available space no longer inadequate this has been brought about, especially in the case of abstracts of papers appearing in the rarer journals and in the less generally read languages. Except in the few cases in which titles are obviously sufficient for all that is suited to *Chemical Abstracts*, the publication of title abstracts has been discontinued. A considerable increase has been made in the number of cuts used with abstracts, especially with patent abstracts. Descriptions of apparatus are often far from satisfactory without drawings.

Italian patents have been abstracted in 1915 for the first time. Italy is the only country of consequence not previously on the list of those whose patents are reviewed in *Chemical Abstracts*.

No. 24 of the 1915 volume contains, in addition to the title pages and author and subject indexes, a list of official abbreviations and a revised list of periodicals abstracted. The latter contains data concerning 671 periodicals, 17 having been added to the 1914 list. Special attention is called to this list as it has been demonstrated that many consider such a list very valuable. No numerical patent index was published in 1915. Suspicion that this index has been little used and that its publication at considerable cost is therefore not justified has been verified by a large amount of evidence gathered. Through the ready coöperation of the assistant editors and abstractors it has been possible to get into the 1915 volume the maximum number of abstracts of available papers, thus making the index very nearly a complete record of the period covered. In the case of joint author patents second and third authors have for the first time been entered as cross-references in the author index.

Preliminary measures have been taken, which it is hoped will lead to the publication of a ten-year index after the completion of the 1916 volume. The success of this project will have a decided influence on the future of the journal. It merits the support of every member of the Society.

The editor can have no words of commendation too cordial for the large amount of excellent work so unselfishly done by the assistant editors and abstractors. The success of the journal depends largely on the assistance rendered by these men. Much credit is due to the office force and the printers for their faithful work all through the year and particularly on the index, the preparation, checking and printing of which is a strenuous task for all. Miss Mary E. Kline, who has had considerable graduate training in chemistry, has taken up the indexing work formerly done by Miss Laura G. Collison. Circumstances have taken Miss Collison from us after five years of creditable service.

Statistics for the separate departments for 1915 are:

	No. pages.	No. abstracts.
Apparatus.....	34.8	251
General and Physical Chemistry.....	286.8	1341
Radioactivity.....	44.1	243
Electrochemistry.....	63.7	380
Photography.....	10.7	69
Inorganic Chemistry.....	70.8	228
Analytical Chemistry.....	84.5	369
Mineralogical and Geological Chemistry.....	94.6	565
Metallurgy and Metallography.....	106.6	725
Organic Chemistry.....	606.4	1155
Biological Chemistry.....	445.0	2524
Foods.....	81.6	454
Water, Sewage and Sanitation.....	70.0	567
Soils and Fertilizers.....	77.5	512
Fermented and Distilled Liquors.....	47.2	233
Pharmaceutical Chemistry.....	89.3	515
Acids, Alkalies, Salts and Sundries.....	19.3	200
Glass and Ceramics.....	27.0	155
Cement and Other Building Materials.....	25.2	169
Fuels, Gas, Tar and Coke.....	52.5	332
Petroleum, Asphalt and Wood Products.....	21.7	141
Cellulose and Paper.....	13.4	123
Explosives and Explosions.....	24.5	127
Dyes and Textile Chemistry.....	29.6	176
Paints, Varnishes and Resins.....	16.9	119
Fats, Fatty Oils and Soaps.....	33.2	201
Sugar, Starch and Gums.....	36.1	171
Leather and Glue.....	20.2	136
Rubber and Allied Substances.....	15.9	109
<hr/>		
Total, not including patents.....	2,549.1	12,290
Patents.....	577.0	6,159
<hr/>		
	3,126.1	18,449
Headings, blanks, cross-references, book titles...	252.9	

3,379

Respectfully submitted,

E. J. CRANE.

### Report of the Editor of the Journal of Industrial and Engineering Chemistry for the Year 1915.

We have produced during the past year 94,900 copies of the *Industrial Journal*. The printing has been divided as follows: 1112 pages of editorial matter equivalent to  $92\frac{2}{3}$  pages per month, and 712 pages of advertising matter, equivalent to  $59\frac{1}{3}$  pages per month. The editorial matter, together with a comparison of this work in previous years, may be summarized as follows:

	1911.	1912.	1913.	1914.	1915.
Pages in editorial section:.....	970	946	1052	1066	1112
Pages in advertising section.....	158	495	604	702	712
Total pages printed.....	1128	1440	1656	1768	1824
Editorials.....	30	19	28	21	25
Original papers.....	140	160	179	187	163
Addresses.....	22	37	57	57	97
Laboratory and Plant articles.....	28	55	43	40	40
Book Reviews.....	36	53	52	72	39
Patents.....	..	..	172	206	286
Current Industrial News items.....	..	..	..	136	154

The additional material for the 1915 volume is made up of Scientific Society reports, Notes and Correspondence, abstracts from Government reports, Personals and general matter.

Respectfully submitted,

M. C. WHITAKER.

## MINUTES OF THE DIRECTORS MEETING.

December 11, 1915.

The Directors of the American Chemical Society met at the Chemists' Club, New York City, on Saturday, December 11, 1915, with President Herty in the chair and all Directors present.

A communication having been received from Congressman Albert Johnson regarding the use of the centigrade scale of temperature measurement in the United States Government publications, the following resolution was passed:

"Resolved, that the Directors of the American Chemical Society are unanimously in favor of the bill presented by Hon. Albert Johnson for the adoption of the centigrade scale of temperature measurement in the United States Government publications, with the understanding that for such time as may be deemed necessary the equivalent temperature in the Fahrenheit scale may follow in parenthesis where the various bureaus concerned deem such inclusion wise."

The Directors voted to sell a microscope and accessories belonging to the Society for the sum of \$15.00, offered by Mr. Buswell through Professor Alexander Smith.

It was voted that \$11.62 be appropriated to the Ames Section, recently authorized by the Council, for their 1915 expenses.

It was voted that \$176.43 be transferred from such funds already appropriated as are still available to cover deficit in the budget of the *Journal of the American Chemical Society*.

It was voted to transfer \$241.10 from the *Chemical Abstracts* budget to cover a deficit of like amount in the *Journal of Industrial and Engineering Chemistry*.

It was voted that in the future the Finance Committee be authorized

to approve all bills in excess of the budget where the bill is a matter of contractual obligation.

It was voted that the Finance Committee, acting with the consent of the President, be authorized to make temporary loans of the general funds of the Society to such fiduciary institutions as may be approved by them.

It was voted that the action of the Finance Committee and the President in reinvesting \$2,000.00 of the Society's funds in New York City bonds 4 $\frac{1}{2}$ %—1965—be approved. The question of reinvesting funds of the Society now invested in Brooklyn Rapid Transit was left to the Finance Committee and President with power.

It was voted that the Finance Committee and President be authorized and instructed to invest \$5,000 from the general funds of the Society in interest-bearing securities approved by them.

The Treasurer's report was received and approved subject to audit.

It was unanimously voted (Dr. Love not voting) to pay \$500 per year salary to the Chairman of the Finance Committee.

In reply to a communication from the Editor of the *Journal of Industrial and Engineering Chemistry* regarding the editorial policy of that Journal, it was voted that the Secretary be instructed to inform the Editor of the *Journal of Industrial and Engineering Chemistry* that the Directors would be glad if he and his board of editors would consider the whole matter of editorial policy at the next general meeting of the American Chemical Society and recommend such action to the Board of Directors as they deem wise.

It was voted that hereafter railroad transportation, sleeper, and meals en route of Directors attending Board of Directors' meetings, other than those held at general meetings of the Society, be paid from Society funds.

It was voted that \$250.00 be appropriated from the general funds of the Society for the expenses of the Committee on coöperation with the United States Government regarding the collating of statistics of foreign commerce in chemicals.

It was voted that the Secretary be directed to request from the Board of Trustees of The Chemists' Club information regarding the expenditure of the income from the Morris Loeb fund already paid to them, and to request a statement regarding their future plans for the Morris Loeb Chemical Type Museum.

By motion of Director Brady it was voted to lay upon the table the proposition of Mr. A. V. Main, which had been presented to the Directors through him.

The following budget for 1916 was then adopted:

## ESTIMATED RECEIPTS.

	1915.	1916.
Secretary's office.....	\$ 76,000	\$ 80,000
Advertisements.....	24,000	26,000
Interest.....	1,200	1,700
	<hr/> \$101,200	<hr/> \$107,700

## ESTIMATED EXPENDITURES.

*Journal of the American Chemical Society:*

	1915.	1916.
Editor's salary.....	\$ 1,000	\$ 1,000
Expenses, including reviews.....	600	560
Printing, including reprints.....	15,400	17,600
Total.....	<hr/> \$ 17,000	<hr/> \$ 19,160

*Chemical Abstracts:*

Editor's salary.....	\$ 1,800	\$ 2,000
Associate editors' salary.....	1,200	1,400
Clerical assistance.....	3,000	2,750
Expenses.....	600	700
Abstractors and department heads.....	8,720	7,550
Printing, including index.....	24,800	21,500
Total.....	<hr/> \$ 40,120	<hr/> \$ 35,900

*Journal of Industrial and Engineering Chemistry:*

Editor's salary.....	\$ 1,000	\$ 1,000
Assistant editors' salaries.....	2,590	2,900
Clerical and office expenses.....	2,100	3,100
Printing, editorial.....	12,400	15,750
Printing, advertisements.....	6,000	7,000
Total.....	<hr/> \$ 24,090	<hr/> \$ 29,750

Advertising manager..... 6,000 6,500

Finance committee, chairman..... 500

*Secretary's office:*

Collection commissions.....	\$ 3,500	\$ 3,500
Expense.....	1,700	1,700
Clerical.....	2,700	2,900

*President's office:*..... 100 .....

*Treasurer's office:*

Salary.....	300	500
Expense.....	400	400
Local sections.....	3,800	4,000
General meetings.....	1,200	1,000
Incidentals.....	800	1,200
Back numbers.....	800	850
Life membership.....	130	.....
Directory.....	.....	500

Total..... \$ 21,430 \$ 23,550

Grand total..... \$102,640 \$108,360

CHARLES L. PARSONS, *Secretary.*

## COUNCIL.

On November 1, a nominating ballot for Directors was sent to the Council, the following being the four leading nominees, which, according to the Constitution, were sent to the Council again for the selection of two:

W. D. Bigelow, W. R. Whitney, Geo. B. Frankforter, A. L. Day.

This ballot was counted by a committee consisting of C. L. Parsons, J. A. LeClerc, and John Johnston.

On November 30 these nominees were sent to the Council, and also the nominees for President and Councilors-at-Large as selected by the membership. (See Proceedings, page 1.) As a result of this ballot, the following officers were elected:

*President:* Charles H. Herty, for the term January 1, 1916, to December 31, 1917.

*Directors:* W. R. Whitney and W. D. Bigelow, for the term January 1, 1916, to December 31, 1918.

*Councilors-at-Large:* George D. Rosengarten, W. D. Bigelow, B. C. Hesse and G. N. Lewis, for the term January 1, 1916, to December 31, 1918. This ballot was counted by a committee consisting of A. L. Day, John Johnston and Charles L. Parsons. CHARLES L. PARSONS, *Secretary*.

### MEMBERS ELECTED BETWEEN NOVEMBER 15 AND DECEMBER 15, 1915.

- Abbott, J. T., 1408 Emerson St., N. W., Washington, D. C.
- Abramovitz, H. L., 450 S. Rebecca St., Pittsburgh, Pa.
- Adams, C. M., c/o Imperial Sugar Co., Sugar Land, Texas.
- Adelson, Louis S., 53 Clarke Ave., Far Rockaway. L. I., N. Y.
- Apmann, Arthur M., 68 Wayne St., Jersey City, N. J.
- Atwood, F. Clarke, 316 Huntington Ave., Boston, Mass.
- Bakke, Oliver Mathias, 209 $\frac{1}{2}$  Lane St., Dallas, Texas.
- Bakken, H. E., 301 Third St., N. E., Little Falls, Minn.
- Banbury, F. H., 577 Central Ave., Orange, N. J.
- Bardorf, Charles F., St. Lawrence Sugar Refineries, Ltd., Maisonneuve, P. Q., Canada.
- Beaver, David J., 310 Victory Ave., Schenectady, N. Y.
- Beecher, Ward, R. F. D. No. 2, Youngstown, Ohio.
- Behr, Alexander W., c/o Russian American Chamber of Commerce, Mjasnitsky Proesd 2, Moscow, Russia.
- Beneker, J. C., Pacific Coast Steel Co., Youngstown Station, Seattle, Wash.
- Bnags, Arvid H., 206 W. Green St., Smethport, Pa.
- Bennett, Charles S., 607 S. Hill St., Los Angeles, Calif.
- Bertolet, Elmer C., 633 Belgrade St., Philadelphia, Pa.
- Bigelow, Charles A., c/o Aetna Explosives Co. Inc., 2 Rector St., New York City.
- Bird, Jr., Charles S., East Walpole, Mass.
- Boehringer, Dr. Rudolph, 112 Second Ave., Newark, N. J.
- Brandon, Harry M., 5 Elizabeth St., Dover, N. J.
- Brewster, G. A., Parkview, Edgemont St., East St. Louis, Ill.
- Brown, Eugene P., 1009 Wertland St., University, Va.
- Brown, Philip, 615 W. Onondaga St., Syracuse, N. Y.

- Brown, Walter J., 290 Rutland Road, Brooklyn, N. Y.  
 Bryan, C. L., Virginia-Carolina Chemical Co., Richmond, Va.  
 Bullens, D. K., Frankford, Philadelphia, Pa.  
 Byers, Louis L., Abrasive Material Co., Bridesburg, Philadelphia, Pa.  
 Campbell, Robert, Nairn Linoleum Co., Newark, N. J.  
 Campbell, Summer E., 670 Highland Ave., Newark, N. J.  
 Carlisle, Paul J., 213 S. Marina St., Prescott, Arizona.  
 Cathcart, Paul H., National Cannery Association, Washington, D. C.  
 Catlett, Richard H., 44 The Fenway, Boston, Mass.  
 Chebotaref, Leo P., Standard Aniline Products Co., Wappinger Falls, N. Y.  
 Clinton, Guy, College of Agriculture, Los Banos, P. I.  
 Collins, Grellet, N., 4111 Walnut St., Philadelphia, Pa.  
 Condit, Percy H., 38 Hamilton St., East Orange, N. J.  
 Coolidge, Walter H., Box 641, Georgetown, Ky.  
 Coyne, James Kitchenman, 2037 North Broad St., Philadelphia, Pa.  
 Currie, William E., 211 14th St., University, Va.  
 Davies, Earle L., 35 Adams St., Akron, Ohio.  
 Davis, R. F., El Segundo, Calif.  
 Davis, Ralph W., 320 Seventeenth Ave., Homestead, Pa.  
 Deterding, Henry C., Crampton Hall, Illinois College, Jacksonville, Ill.  
 Dinsmore, Ray P., 22 So. Maple St., Akron, Ohio.  
 Dixon, Frederick W., 409 Pine St., Jamestown, N. Y.  
 Dodds, Eugene H., 311 So. Ridgeland Ave., Oak Park, Ill.  
 Downing, George Valentine, Elsmere, Del.  
 Downing, R. C., 30 W. 70th Place, Chicago, Ill.  
 Dubbs, C. P., 1743 Wesley Ave., Evanston, Ill.  
 Dunphy, Raymond A., Mellon Institute, Pittsburgh, Pa.  
 Durham, Charles, 2912 Prairie Ave., Chicago, Ill.  
 Ellinger, Louis J., 11 East 68th St., New York City.  
 Engles, Charles Robert, 3320 W. Huntingdon St., Philadelphia, Pa.  
 Essex, Harry, Mellon Institute, Pittsburgh, Pa.  
 Fay, Thornwell, c/o Union Sulphur Company, Sulphur, La.  
 Fisher, Harry H., Ridley Park, Pa.  
 Fosgate, Neal R., 419 Pearl St., Burlington, Vt.  
 Foster, Goodwin L., Sharon, Mass.  
 Fowler, Edward J., c/o Pacific Foundry Co., 18th and Harrison Sts., San Francisco, Calif.  
 Frazier, Thos. A., 1302 Sheffield St., Pittsburgh, Pa.  
 Frusher, Tom, 60 Federal St., Boston, Mass.  
 Fry, J. M., 262 Dixon Place, Akron, Ohio.  
 Gahl, Rudolf, Inspiration Consolidated Copper Co., Globe, Ariz.  
 Gailey, Andrew J., 2112 Federal St., Philadelphia, Pa.  
 Gallagher, J. A., North Wilmington, Mass.  
 Gallup, Wm. Arthur, North Adams, Mass.  
 Geist, H. H., 604 N. 3rd St., Pottsville, Pa.  
 Githens, Frank Weeder, c/o Penn. Wire Glass Co., Dunbar, Pa.  
 Goerner, Alfred, 542 Kosciusko St., Brooklyn, N. Y.  
 Goldsmith, C. H., Orono, Maine.  
 Grantham, R. I., c/o Sharpe & Dohme, Baltimore, Md.  
 Gubelmann, Dr. Ivan, 1800 S. Second St., St. Louis, Mo.  
 Hammett, Louis P., Hollis 24, Cambridge, Mass.



- Harris, Eloise J., Hardin College, Mexico, Mo.  
 Hathorne, Wade, 1003 W. Illinois St., Urbana, Ill.  
 Helwig, Edward Leslie, 1810 N. 26th St., Philadelphia, Pa.  
 Hendrickson, Norman, 48 East Stratford Ave., Lansdowne, Pa.  
 Holland, William Rankin, Welsbach Co., Gloucester, N. J.  
 Horton, Frederick W., c/o U. S. Bureau of Mines, Denver, Colo.  
 Huffman, R. G., 2636 Q Street, London, Nebr.  
 Hultman, Ivar N., 302 W. Springfield Ave., Champaign, Ill.  
 Humphrey, Harry Lyman, 313 Wait Ave., Ithaca, N. Y.  
 Hunt, Frank Shepard, 216 Greene Ave., Brooklyn, N. Y.  
 Huntley, H. W., Mellon Institute, Pittsburgh, Pa.  
 Hurwitz, Benj., 42-44 Salem St., Boston, Mass.  
 Ingram, Jr., T. J., Box 440, University, Va.  
 Jarvis, Ernest G., c/o Canadian Inspection and Testing Laboratories,  
 Montreal, Canada.  
 Jennings, Harry J., 1312 Tatnoll St., Wilmington, Del.  
 Johnson, C. R., 1508 Preston Ave., Akron, Ohio.  
 Johnson, Robert L., Stephenson Charcoal Iron Co., Wells, Mich.  
 Johnston, William S., 542 West 112th St., New York City.  
 Jones, Leo D., c/o Union Powder Corp., Parlin, N. J.  
 Jones, R. U., 215 N. Murray St., Madison, Wisc.  
 Jordan, Wm. G., 409 So. Linn St., Iowa City, Iowa.  
 Kakiuchi, Dr. Samuro, 164 Mansfield St., New Haven, Conn.  
 Kennicott, Cass L., Chicago Heights, Ill.  
 Kersey, Kenneth S., 512 N. 20th St., Omaha, Nebr.  
 Kimball, J. Willard, 1120 Linde Ave., Baltimore, Md.  
 Klipstein, Ernest C., 93 Prospect St., E. Orange, N. J.  
 Knoch, Franklin E., Florence, Colo.  
 Koster, F. William, 202 E. 8th St., Chester, Pa.  
 Kramer, Elmer C., 3302 Monteith Ave., Cincinnati, Ohio.  
 Kremers, Harry C., 1102 W. Springfield Ave., Urbana, Ill.  
 Kutz, Milton, 941 Drexel Bldg., Philadelphia, Pa.  
 Lebowitz, Samuel, 1201 Epiphany St., Pittsburgh, Pa.  
 Leiby, Fred E., 325 Cutler Bldg., Rochester, N. Y.  
 Letourneau, Marius, 2097 Notre Dame St., West, Montreal, Canada.  
 Libby, Lucien Taylor, H. H. Hall, Orono, Maine.  
 Line, Willard R., 50 Rowley St., Rochester, N. Y.  
 Lipman, Chas. B., Budd Hall, Berkeley, Calif.  
 Little, Herman J., Mellon Institute, Pittsburgh, Pa.  
 Lohr, Vergil Claybourne, 104 Sherman St., Joliet, Ill.  
 Loud, Warren S., 1030 N. Branch St., Chicago, Ill.  
 Lybeck, Robert F., 36 Highland Ave., Everett, Mass.  
 Lyon, Goffrey A., Clyde, Ohio.  
 Mahre, Alfred, Sioux Falls, So. Dak.  
 Maier, Chas. G., 463 Portage Rd., Niagara Falls, N. Y.  
 Mali, Harry E., 3600 Greenview Ave., Chicago, Ill.  
 Mallinson, Herbert C., Box 873, Maynard, Mass.  
 Markel, Paul D., 1120 Linden Ave., Baltimore, Md.  
 Melville, William, St. Marys, Pa.  
 Merkle, A. H., 644 S. 51st St., Philadelphia, Pa.  
 Merz, August, c/o The Heller & Merz Co., Newark, N. J.  
 Meyer, M. I., 1234 Independence Blvd., Chicago, Ill.

- Miller, Dr. E. C. L., Medical College of Va., Richmond, Virginia.  
 Miller, Harry L., 4522 Forbes St., Pittsburgh, Pa.  
 Miller, R. W., c/o College Club, Manhattan, Kans.  
 Miyake, Koji, c/o Mrs. S. E. Good, 2212 Channing Way, Berkeley, Calif.  
 Moore, Stanley B., Bacchus, Utah.  
 Morgan, D. Glenn, 416 West St., Stillwater, Okla.  
 Morosoff, P. A., 1014 Flatiron Bldg., New York City.  
 Morris, Paul R., Room 20, Y. M. C. A., Mt. Vernon, Ohio.  
 Morrison, Raymond A., 264 Columbia Ave., Palmerton, Penna.  
 Morse, Earle H., Aubert Hall, Orono, Maine.  
 Morton, Harold A., Mellon Institute, University of Pittsburgh, Pittsburgh, Pa.  
 Morton, Isadore, 1520 South Ridgeway Ave., Chicago, Ill.  
 Moss, Lowell R., 1109 Jefferson St., Wilmington, Del.  
 Murphy, Walter B., 4211 Sansom St., Philadelphia, Pa.  
 Mutscheller, Arthur, 112 East 77th St., New York City.  
 Nash, Geo. H., Virginia-Carolina Chemical Co., Richmond, Va.  
 Neusbaum, C. A., Mellon Institute, Pittsburgh, Pa.  
 Naylor, John Thomas, 604 S. State St., Ann Arbor, Mich.  
 Naylor, Ralph B., 73 Lute St., Springfield, Mass.  
 O'Brien, W. G., 595 N. Howard St., Akron, Ohio.  
 O'Rourke, Francis, A. T. D. House, Orono, Maine.  
 Palm, Otto G., 41 Colborne St., Toronto, Canada.  
 Parker, William H., 37 Collins Rd., Waban, Mass.  
 Patterson, C. A., Woodbury, N. J.  
 Pease, Robert N., 468 College St., Burlington, Vt.  
 Phelps, Ferdinand Z., Sigma Chi House, Orono, Maine.  
 Pinnock, Douglas R., c/o Nucoa Butter Co., Bayonne, N. J.  
 Porteous, Edw. J., P. O. Box 432, Long Beach, Calif.  
 Putnam, Willis S., Womens College of Delaware, Newark, Del.  
 Quick, Oscar, 242 S. 18th Ave., Maywood, Ill.  
 Ramsay, Harvey W., 1395 Temple Place, St. Louis, Mo.  
 Ransohoff, Dr. Fritz, 2425 Lakeview Ave., Baltimore, Md.  
 Reinertsen, B. Reynold, Elk Point, So. Dak.  
 Richardson, George Oliver, Room 403, Y. M. C. A., Lowell, Mass.  
 Roberts, Thomas H., 283 Pitman St., Providence, R. I.  
 Rogers, Homer, 127 West 17th St., Wilmington, Del.  
 Rupright, Howard J., Midland, Mich.  
 Russell, Walter C., 176 N. Sandusky St., Delaware, Ohio.  
 Ryland, Edward, Virginia-Carolina Chemical Co., Richmond, Va.  
 Sanders, W. W., 472 East Buchtel Ave., Akron, Ohio.  
 Sayre, Ralph, Bureau of Chemistry, Washington, D. C.  
 Schill, Dr. Emil, 52 East 41st St., New York City.  
 Scott, Frederick Hughes, Physiological Dept., University of Minnesota, Minneapolis, Minn.  
 Sease, V. B., 1120 Linden Ave., Baltimore, Md.  
 Shaw, David F., 294 Benefit St., Providence, R. I.  
 Shive, John W., Exp. Station, N. J. Agric. College, New Brunswick, N. J.  
 Shively, R. R., Mellon Institute, Pittsburgh, Pa.  
 Skjold, Eimar, Erith Oil Works, Ltd., Erith near London, England.

Smith, Albert E., c/o New Bedford & Agawam F. Co., East Wareham, Mass.

Smith, Arthur L., 224 S. Millvale Ave., Pittsburgh, Pa.

Smith, Charles M., 309 Tennessee Ave., N. E., Washington, D. C.

Smith, Dillon F., Mellon Institute, Pittsburgh, Pa.

Solomon, H., Agricultural College, Miss.

Stebbins, Jr., James H., 50 East 41st St., New York City.

Stewart, Dr. Jeffrey, 2524 South Cleveland Ave., Philadelphia, Pa.

Stickels, A. E., Cicero, Ind.

Sutton, Park N., Midland, Mich.

Szendery, Louis E., 62 W. 10th Ave., Columbus, Ohio.

Ten Broeck, C. W., Parlan, N. J.

Terry, Philip B., 2567 Bedford Ave., Brooklyn, N. Y.

Theel, Percival, Jarrettsville, Pa.

Thurman, B. H., c/o Capitol Refining Co., Washington, D. C.

Titus, Esbon Y., 1004 W. Washington Ave., Madison, Wisc.

Tressel, Jos. J., 1811 Josephine St., Cincinnati, Ohio.

Troxler, Bernhart, 2 Baker Ave., Dover, N. J.

Truesdell, Benj. W., 412 N. Emporia Ave., Wichita, Kans.

Van De Vrede, R. N., 801 Price St., Savannah, Ga.

Van Kirk, Jr., Robert W., 237 Beacon St., Boston, Mass.

Verity, Ben, 550 Hood St., Fall River, Mass.

Vickers, Charles, 633 Thirteenth St., Niagara Falls, N. Y.

Voris, Clarence R., Fairbury, Ill.

Wales, Jr., Horatio, Fernald Hall, Columbia University, New York City.

Weaver, Ralph B., R. F. D. No. 2, Puyallup, Wash.

Webster, Jas. C., 1283 Fry St., Lakewood, Ohio.

Weirick, H. C., Timken Roller Bearing Co., Canton, Ohio.

Will, E. G., Experiment Station, Fayetteville, Ark.

Willkie, H. F., Fajardo, Porto Rico.

Woolford, C. S., 3031 St. Paul St., Baltimore, Md.

Wrenshall, Dr. Richard, 240 Academy Ave., Sewickley, Pa.

Wright, Alfred, c/o Rochester Germicide Co., Rochester, N. Y.

Wright, Geo. T., 2718 Lincoln Way, Ames, Iowa.

Young, Charles O., 142 S. Anderson St., Los Angeles, Calif.

Ziegler, William A., St. Marks School, Southboro, Mass.

## MEETINGS OF THE SECTIONS.

[Full accounts of all meetings should be sent to Secretary Charles L. Parsons, Box 505, Washington, D. C.]

### LEXINGTON SECTION.

The 26th regular meeting was held November 22. Program: "The Effect of the European War on Drug Supplies," by L. A. Brown; "The Stability of Silver Fulminate under Water," by A. M. Peter.

The December meeting was held December 8. Program: "The Translocation of the Mineral Constituents of Certain Seeds during Growth," by G. D. Buckner; "A Review of the Literature on the Distribution and

Sources of Iodine in Plant and Animal Life," by P. L. Blumenthal. The officers for 1916 were elected, as follows: C. A. Nash, *Chairman*; O. M. Shedd, *1st Vice-Chairman*; Mary Sweeny, *2nd Vice-Chairman*; P. L. Blumenthal, *Secretary-Treasurer*; F. E. Tuttle, *Councilor*.

LLOYD C. DANIELS, *Secretary*.

#### CHICAGO SECTION.

The regular meeting was held December 8. Program: "The Manufacture of Gasoline and Benzole Toluene from Petroleum and other Hydrocarbons," by Walter F. Rittman.

A special-memorial meeting was held in honor of Dr. John Ulric Nef, December 17. Dr. Lauder W. Jones spoke on "The Scientific Work Developed by Dr. Nef."

D. K. FRENCH, *Secretary*.

#### AMES SECTION.

The 2nd regular meeting was held December 2. Program: "Peculiarities in the Chemistry and Physics of Silicate Industries," by Homer F. Staley.

W. G. GARSSLER, *Secretary*.

#### MARYLAND SECTION.

At the regular meeting held November 13, the following officers were elected for 1916: C. P. Van Gundy, *Chairman*; E. E. Reid, *Vice-Chairman*; F. M. Boyles, *Secretary-Treasurer*; S. T. Powell, W. W. Randall, *Executive Committee*.

The 9th regular meeting was held December 11. Program: "Partition or Neutral Solubility," by E. E. Reid and B. B. Wroth; "Methods of Toxicological Examinations," W. B. D. Penniman.

FRANK M. BOYLES, *Secretary*.

#### LOUISIANA SECTION.

The 89th regular meeting was held November 19. Program: "Some Aspects of Illuminating Gas Manufacture," C. Hartogh; "Journal Reviews," Philip Asher.

The 90th regular meeting was held December 17. Program: "The Manufacture and Usages of White Lead," and "The Crime of Carelessness" (motion pictures).

F. W. LIEPSNER, *Secretary*.

#### WISCONSIN SECTION.

The November meeting was held November 17. Professor J. H. Walton, Jr., spoke on "The Influence of Impurities on the Rate of Growth of Ice Crystals."

The December meeting was held December 8. Professor R. A. Millikan, of the Physics Department of the University of Chicago, spoke on "The Nature of Radiant Energy."

The annual meeting was held December 10. The following officers were elected for 1916: E. V. McCollum, *Chairman*; P. W. Carleton, *Vice-*

*Chairman*; L. A. Augspurger, *Secretary*; E. Truog, *Treasurer*; R. Fischer, *Councilor*.

A. E. KOENIG, *Secretary*.

#### CINCINNATI SECTION.

At the meeting held November 10 the following officers were elected for 1916: C. Bahlmann, *President*; F. O. Clements, *1st Vice-President*; H. S. Fry, *2nd Vice-President*; E. K. Files, *Secretary-Treasurer*; L. W. Jones, *A. Campbell, Councilors*.

STEPHEN J. HAUSER, *Secretary*.

#### UNIVERSITY OF MICHIGAN SECTION.

The November meeting was held November 23. Program: "A Study of the Hydrochloric Acid Concentration Cell with Respect to Activity and Concentration, Boundary Potential and Transparent Members," by A. L. Ferguson. The following officers were elected to serve for 1916: D. M. Lichty, *Chairman*; H. H. Willard, *Secretary-Treasurer*; W. J. Hale, *Councilor*; W. B. Peet, M. Gornberg, W. G. Smeaton, *Executive Committee*.

The December meeting was held December 9. Program: "Ferrotungsten as an Industry," by R. L. Sessions.

H. H. WILLARD, *Secretary*.

#### NEW YORK SECTION.

The regular meeting was held December 10, in conjunction with the American Electrochemical Society. Program: "University and Industry," Richard C. Maclaurin, Henry P. Talbot, William H. Walker, Arthur D. Little, all representing Massachusetts Institute of Technology; "The Naval Consulting Board of the United States," by L. H. Baekeland and W. R. Whitney. The following councilors were elected for 1916: Charles Baskerville, S. R. Church, B. C. Hesse, C. M. Joyce, T. B. Wagner, A. C. Langmuir, K. G. Mackenzie, J. M. Matthews, T. J. Parker, I. F. Stone, J. E. Teeple.

C. M. JOYCE, *Secretary*.

#### PUGET SOUND SECTION.

The following officers for 1916 were elected at the meeting held November 20: E. A. Dieterle, *Chairman*; Rex Smith, *Vice-Chairman*; H. L. Trumbull, *Secretary*; J. E. Bell, *Treasurer*; H. K. Benson, *Councilor*.

H. L. TRUMBULL, *Secretary*.

#### UNIVERSITY OF ILLINOIS SECTION.

The following officers for 1916 were elected at the meeting held November 15: W. A. Noyes, *Chairman*; John C. Hessler, *Vice-Chairman*; G. D. Beal, *Secretary*; B. S. Hopkins, *Treasurer*; E. W. Washburn, S. W. Parr, *Councilors*.

G. D. BEAL, *Secretary*.

#### NORTHEASTERN SECTION.

The regular meeting was held December 10. Program: "The Chemistry of Amorphous Solids," by Warren K. Lewis. The following officers were

elected for 1916: F. H. Thorp, *President*; C. L. Gagnebin, *Vice-President*; E. B. Spear, *Secretary*; H. C. Lythgoe, *Treasurer*; Roger Adams, F. Bonnet, Jr., G. J. Esselen, Jr., R. B. Earle, G. W. Harris, *Executive Committee*; Henry Fay, W. L. Jennings, Grinnell Jones, W. K. Robbins, H. P. Talbot, *Councilors*.

GRINNELL JONES, *Secretary*.

#### WESTERN NEW YORK SECTION.

A meeting was held December 8 in conjunction with the American Electrochemical Society. Program: "Electrons, Atoms, and Energy Quanta," by Dr. Saul Dushman.

RAY H. WHITE, *Secretary*.

#### CALIFORNIA SECTION.

The eighty-seventh regular meeting was held November 23. Program: "The Equilibrium of Oxidation Reactions," by Prof. Arthur A. Noyes; "Hydrocarbon Reactions at High Temperature," by Dr. Walter F. Rittman.

BRYANT S. DRAKE, *Secretary*.

#### OREGON SECTION.

The annual meeting was held November 27. Program: "Some Modern Views of Matter," by W. C. Morgan.

F. A. OLMSTEAD, *Secretary*.

#### DETROIT SECTION.

The regular meeting was held December 16. The program consisted of three papers as follows:

Wilbur L. Scoville, "Formaldehydized Capsules." Discussion led by C. H. Briggs, F. O. Taylor and L. B. Hayward.

Dr. Charles H. Oakman, "Dental Surgery." Discussions by Drs. Stephenson, Hayward and Clark.

John W. M. Bunker, "A Piece of Cheese." Discussions by Dr. Diack, F. O. Robison and H. C. Hamilton.

EDW. J. GUTSCH, *Secretary*.

#### MINNESOTA SECTION.

The Section met Nov. 19. Program: "The Nature of the Proteins Extracted from Wheat Flour by Various Processes," by Prof. C. H. Bailey; "Recent Advances in Chemo-therapy," by Dr. A. D. Hirschfelder.

The Section met December 17. Program: "Flavoring Extracts and Baking Powders," by Wm. Kennedy; "The Polymerization of China Wood Oil," by Carl Schuman; "The Swelling of Rubber in Organic Liquids," by I. H. Derby.

STERLING TEMPLE, *Secretary*.

#### SOUTHERN CALIFORNIA SECTION.

The regular meeting was held November 18. The paper of the evening was presented by Mr. L. H. Buck, Chemist for the City Dye Works, entitled, "Carbon Tetra-chlorid."

H. L. PAYNE, *Secretary*.

## NEW HAVEN SECTION.

The regular meeting was held December 10. Professor C. E.-A. Winslow, Anna M. R. Lauder Professor of Public Health in the Yale Medical School, delivered a lecture on the subject, "The Disposal of City Sewage."

GEORGE S. JAMIESON, *Secretary*.

## ROCHESTER SECTION.

The regular meeting was held December 6. Dr. Frank K. Cameron, Bureau of Soils, Dept. of Agriculture, Washington, D. C., gave a talk on "American Resources in Fertilizer Materials."

H. H. TOZIER, *Secretary*.

## WASHINGTON SECTION.

The Section held a special meeting December 8. The meeting was held through the courtesy of the National Rivers and Harbors Congress.

The 254th meeting of the Society was held December 16. Program: G. K. Burgess, of the Bureau of Standards, "Some Examples of Metal Failures" (illustrated); B. McCollum, of the Bureau of Standards, "Chemical Factors Affecting Electrolytic Corrosion in Soils and Reinforced Concrete;" R. B. Dole, of the Geological Survey, "The Action of Natural Waters on Boilers."

E. C. McKEEVER, *Secretary*.

## MILWAUKEE SECTION.

There was an extra meeting of the Engineers Society of Milwaukee held under the auspices of the Milwaukee Section of the American Chemical Society, December 3. Professor S. W. Parr, of the University of Illinois, delivered an illustrated talk on, "Development in the Marketing of Coal--Specifications, Storage, etc."

BEN L. SALOMON, *Secretary*.

## CLEVELAND SECTION.

The Section held its regular December meeting December 13. Dr. A. G. Worthing, of the Nela Research Laboratory of the General Electric Co., addressed the Society on, "The Electron Theory and Some of Its Applications."

A. F. O. GRIMMANN, *Secretary*.

## NEBRASKA SECTION.

The December meeting was held December 11. Chancellor Samuel Avery, of the University of Nebraska, gave an address on "Our National Chemical Industries." The following officers for 1916 were elected: F. W. Upson, *President*; J. S. Cutter, *Vice-President*; H. M. Plum, *Secretary-Treasurer*; Samuel Avery, *Councilor*; H. H. Hosford, Geo. Borrowman, C. A. Morrow, *Executive Committee*.

H. M. PLUM, *Secretary*.

## COLUMBUS SECTION.

The November meeting was held November 23. Professor W. L. Evans lectured on "The Life and Work of John Ulric Nef."

W. J. McCAUGHY, *Secretary*.

## PHILADELPHIA SECTION.

The regular meeting was held December 16. Program: "The Decomposition of Hydrocarbon Oils under High Temperatures and Pressures, and the Industrial Applications of the Process," by Dr. Walter F. Rittman.

C. S. BRINTON, *Secretary*.

## VIRGINIA SECTION.

The December meeting was held December 10. Through the courtesy of the faculty of Richmond College, the Section heard Prof. W. S. Franklin, of Columbia University, lecture on "Some Mechanical Analogies in Electricity and Magnetism."

W. A. BURROWS, *Secretary*.

## PITTSBURGH SECTION.

The 21st regular meeting was held November 18. Program: "Demonstration of a Portable Gas Detector," by G. A. Burrell; "The Mechanism of Corrosion," by James Aston; "The Manufacture of Refractories," by R. H. H. Pierce.

The 122nd regular meeting was held December 16. Program: "Hydrometallurgy of Copper," by Raymond F. Bacon; "The Removal of Iron from a Municipal Water Supply," by S. Buka.

W. C. COPE, *Secretary*.

## CONNECTICUT VALLEY SECTION.

The 36th regular meeting was held December 11. Program: "Smoking Opium in the United States," by H. L. Thompson; "The Rittman Gasoline Process," by E. C. Stone.

R. J. MARSH, *Secretary*.

## DECEASED MEMBERS.

Richard E. Berger, Cleveland, O. Died November 25, 1915.

Siegfried H. Hartig, Pittsburgh, Pa. Died November 15, 1915.

David W. Lewis, Cleveland, O. Died November 24, 1915.

James H. Pettit, Urbana, Ill. Died November, 1915.

Anton Vorisek, New York City. Died December 3, 1915.



# Proceedings.

## COUNCIL.

President Herty appointed Dr. Charles Baskerville to represent the A. C. S. on the Joseph H. Holmes Memorial Committee with Dr. S. S. Voorhees as alternate.

### Treasurer's Report.

Cash on Hand, December 1, 1914 .....			\$7,582.82
	RECEIPTS.	1914	1915
Secretary's Office .....		\$76,805.97	\$80,189.22
Advertising .....		25,056.06	26,206.31
			<u>\$106,395.53</u>
Interest:			
Farmers' Loan & Trust Co. (Reg. A/c)...	\$ 163.33	175.58	
First National Bank of Yonkers.....	108.25	81.60	
Certificates of Deposit.....	343.21	333.33	
			<u>\$590.51</u>
Interest on Investments:			
Atlas Portland Cement.....		120.00	
Ill. Cent., Chi., St. Louis and New Orleans		175.00	
Hocking Valley Ry.....		45.00	
Nor. Pac.-Grt. Nor. C. B. & Q.....		40.00	
Brooklyn Rapid Transit.....		50.00	
N. Y. Con. R. R.....		45.00	
U. S. Steel Corp.....		500.00	
City of N. Y.....		70.00	
			<u>\$1,045.00</u>
Total.....	\$ 780.00		
Interest on Special Funds:			
Life Membership Fund:			
Mutual Telegraph.....		100.00	
City of N. Y.....		35.00	
Emigrant Indus. Savings Bank.....		19.78	
			<u>\$154.78</u>
Total.....	\$ 145.82		
Morris Loeb Fund:			
Ill. Cent., Chi., St. Louis and New Orleans		250.00	
N. Y. Con. R. R.....		225.00	
Brooklyn Rapid Transit.....		250.00	
Nor. Pac.-Grt. Nor. C. B. & Q.....		200.00	
Hocking Valley R. R.....		225.00	
Farmers' Loan & Trust Co.....		19.99	
			<u>\$1,169.99</u>
Total.....	\$ 1,037.35		
Bond Investment Paid.....			\$2,000.00
Chemical Abstracts:			
Abstractors.....			21.80
Secretary's Office:			
Expense.....			.10
			<u>\$118,960.53</u>

	DISBURSEMENTS. 1914	1915	
<i>Journal</i> , Editor's salary.....	\$ 1,000.00	\$ 1,000.00	
Assistance to Editor.....	360.00	360.00	
Expense.....	129.86	145.15	
Printing, Editorial.....	13,410.48	14,883.88	
Printing, Advertisements.....	367.89	328.05	
Reprints.....	936.35	1,129.67	
Reviews.....	34.00	....	
	<hr/>	<hr/>	
	\$16,238.58		\$17,846.75
<i>Chemical Abstracts</i> , Editor's salary.....	\$ 1,062.45	\$ 1,837.50	
Associate Editors.....	2,837.39	1,202.50	
Assistance to Editor.....	2,520.64	2,647.32	
Expense.....	668.96	597.87	
Abstractors.....	8,448.41	7,211.52	
Printing, Editorial.....	23,573.04	20,850.38	
Printing, Advertisements.....	472.70	473.53	
	<hr/>	<hr/>	
	\$39,583.59		\$34,820.62
<i>Journal Ind. and Eng. Chem.</i> , Editor's salary..	\$ 1,000.00	\$ 1,000.00	
Assistant Editor's salary.....	1,533.33	1,779.17	
Expense.....	954.85	1,241.59	
Clerical.....	1,156.00	1,691.00	
Reprints.....	1,221.87	1,853.94	
Printing, Editorial.....	11,211.27	12,178.00	
Printing, Advertisements.....	5,355.94	5,703.35	
	<hr/>	<hr/>	
	\$22,433.26		\$25,447.05
Advertising, Commission.....	\$ 6,339.27	\$ 6,625.69	
Expense.....	24.06	122.30	
	<hr/>	<hr/>	
			\$ 6,747.99
Secretary's Office, Clerical.....	\$ 2,558.23	\$ 2,698.88	
Expense.....	1,748.60	1,693.82	
Commission.....	3,500.00	3,500.00	
	<hr/>	<hr/>	
			\$ 7,892.70
Treasurer's Office, Salary.....	\$300.00	\$300.00	
Expense.....	400.00	400.00	
	<hr/>	<hr/>	
			\$700.00
General Meetings.....	\$ 385.60		\$ 1,019.38
Local Sections.....	3,726.50		3,978.03
Back Numbers.....	830.63		855.91
Incidentals.....	353.17		453.80
President's Office.....	50.07		71.41
Bond Investment.....	5,184.46		7,157.28
Directory.....	480.32		....
Life Membership.....	....		130.00
Life Membership Fund.....	....		154.78
Morris Loeb Fund.....	....		1,169.99
Balance:			
Farmers' Loan & Trust Co.....		\$10,355.33	
First National Bank, Yonkers.....		159.51	\$10,514.84
		<hr/>	
			\$118,960.53

## BALANCE SHEET.

## ASSETS.

## Special Investment Fund:

Brooklyn Rapid Transit 6 yr. 5% Gold Notes.....

Nor. Pac.-Grt. Ner. C. B. &amp; Q. 4% Bonds.....

Hocking Valley Ry. 1st Cons. Mte. 4 1/2% Gold

Bond.....

N. Y. Con. R. R. 1st Mte. 4 1/2% Gold Bond.....

Ill. Cent. R. R. Co. &amp; Chicago, St. Louis &amp; New

Orleans R. R. Joint 1st Mte. Refunding Mte. 5%  
Bond.....

\$10,000, U. S. Steel Corp. Gold Bonds due 1963...

\$2,000, Atlas Portland Cement Co. Bonds 6 7/8%...

\$5,000, Ill. Cent., Chicago, St. Louis &amp; New Orleans

Series A Joint First Refunding Mte. due 1963...

\$2,000, Corporate Stock City of N. Y. 4 1/2%.....

Life Membership Fund:

\$2,000, 6% Mutual Telegraph Bonds

due 1941.....

\$1,000, 3 1/2% N. Y. City Gold Bonds

due 1928.....

Emigrant Industrial Savings Bank.....

Morris Loeb Fund:

Cash on Hand.....

Farmers' Loan &amp; Trust Co. ....

First National Bank, Yonkers.....

## LIABILITIES.

December 1, 1915.

Life Membership Fund.....

\$3,676.93

Morris Loeb Fund.....

26,382.34

Excess of Assets over Liabilities.....

34,820.06

\$10,075.00

2,040.00

5,052.78

2,104.50

\$2,128.33

895.00

653.60

\$3,676.93

\$26,382.34

\$10,355.33

\$159.51

\$10,514.84

\$64,870.33

\$64,870.33

MORRIS LOEB FUND

December 1, 1915.

\$25,212.35

Balance, December 1, 1914 .....

Bonds Purchased:

\$5,000, Brooklyn Rapid Transit 5% Note.....	
\$5,000, Nor. Pac.-Gt. Nor. Joint 4% .....	
\$5,000, Hocking Valley 4 <sup>1</sup> / <sub>2</sub> %.....	
\$5,000, N. Y. Con. R. R. 4 <sup>1</sup> / <sub>2</sub> %.....	\$25,151.52
\$5,000, Ill. Cent. & Chicago, St. Louis and New Orleans 5%.....	
Balance, Cash on Hand.....	1,230.82

24

\$26,382.34

\$26,382.34

Life Membership Fund:

Balance, December 1, 1914.....

\$3,522.15

Interest Received.....

154.78

Bonds Purchased:

\$1,000 3 <sup>1</sup> / <sub>2</sub> % N. Y. City Gold Bonds, due 1928.....	\$ 895.00
\$2,000, 6% Mutual Telegraph Bonds, due 1941.....	2,128.33

Balance, Cash on hand .....

\$ 3,023.33  
653.60

\$ 3,676.93

\$ 3,676.93

The above Treasurer's Report has been duly audited by J. Yalden Co., and report made to the Finance Committee.

**MEMBERS ELECTED BETWEEN DECEMBER 15, 1915, AND JANUARY 15, 1916.**

Albrecht, P. Gerhard, 1353 Central Ave., Cleveland, Ohio.  
 Anderson, Arvid E., Lockport, Ill.  
 Anderson, George Alfred, 103 University St., Lafayette, Ind.  
 Anderson, Myron S., Chem. Dept., Iowa State College, Ames, Iowa.  
 Appelbaum, A. I., 1110 Seventeenth St., Altoona, Pa.  
 Arnesen, M. J., 280 Eleventh St., Milwaukee, Wisc.  
 Au, Kei-Wai, Hartley Hall, Columbia University, New York City.  
 Ayer, Arthur W., Argo, Ill.  
 Babcock, George S., 200 Willard Ave., Ithaca, N. Y.  
 Bailey, J. Stanley, 501 Irving Ave., Syracuse, N. Y.  
 Barescheer, Wm. J., 126 Prospect St., Merchantville, N. J.  
 Barnard, Arthur E., 71 Verndale Ave., Providence, R. I.  
 Barnett, Abraham, 91 Hooper St., Brooklyn, N. Y.  
 Barnewolt, A. J., 200 N. Vernon Ave., Pasadena, Calif.  
 Bartlett, Edward P., Claremont, Calif.  
 Beckman, Elmer H., 10919 Churchill Ave., N. E., Cleveland, Ohio.  
 Bellis, Arthur E., 60 Avon Place, Springfield, Mass.  
 Berger, David, 1349 So. Second St., Philadelphia, Pa.  
 Bernhard, Adolph, 438 Central Park W., New York City.  
 Best, Leonard E., 291 Harvard St., Brookline, Mass.  
 Betz, L. Drew, 6424 N. Woodstock St., Germantown, Philadelphia, Pa.  
 Birk, Glover, 308 S. Broadway Park, Lexington, Ky.  
 Blish, Morris J., 1833 Chestnut St., Philadelphia, Pa.  
 Block, J. W., cr. Superior Chemical Co., Joliet, Ill.  
 Blodgett, Wm. Nelson, 230 Highland Ave., Trenton, N. J.  
 Bowers, Clinton R., 53 Wilson St., Portland, Maine.  
 Bowers, W. G., Ellendale, N. Dak.  
 Boyd, Oscar F., Wilmington, Ohio.  
 Braham, Jos. M., University of Illinois, Urbana, Ill.  
 Bramlet, Hubert B., 917 W. Green St., Urbana, Ill.  
 Brewster, Ray Q., 1428 Tenn. St., Lawrence, Kans.  
 Brickman, C. L., 10516 Wilbur Ave., Cleveland, Ohio.  
 Brooks, Percival C., 239 W. 16th St., Chicago Heights, Ill.  
 Brown, Edith L., Gazelle, Calif.  
 Bryant, Charles S., Dragon Str., Rigaud, Que., Canada.  
 Burns, Robt. M., 1012 Fourteenth St., Boulder, Colo.  
 Burrough, S. Lester, 32 Fithian Ave., Merchantville, N. J.  
 Burrows, Lincoln, 21 Augustine St., Rochester, N. Y.  
 Boyer, Sylvester, 2735 Jackson, Corvallis, Oregon.  
 Butterfield, E. E., 135 East 34th St., New York City.  
 Cade, Arthur R., 1810 Portland Ave., Minneapolis, Minn.  
 Cady, Harold S., 44 Willow St., Waterbury, Conn.  
 Calbeck, J. H., 603 W. Bridge, Blackwell, Okla.  
 Campbell, H. L., Box 10, Marine City, Mich.  
 Campbell, Hugh Morton, 3163 Niles Ave., Mt. Lookout, Cincinnati, Ohio.  
 Carlton, Henry A., 3600 N. Second St., St. Louis, Mo.

- Caswell, E. W., 436 E. Buchtel Ave., Akron, Ohio.  
 Chambers, A. D., 1519 Franklin St., Wilmington, Del.  
 Clay, Cassius L., La. State Board of Health, New Orleans, La.  
 Close, Harold W., Graduate College, Princeton, N. J.  
 Coakley, M. T., cr. General Crushed Stone Co., Easton, Pa.  
 Coblentz, M. H., 24 Navarro Flats, Macon, Ga.  
 Codwise, Philip W., 8 Clifton Park, Melrose Highlands, Mass.  
 Cole, Raymond K., 1641 Thomas Ave., Baltimore, Md.  
 Coleman, John, 3936 Delmar Blvd., St. Louis, Mo.  
 Cope, William Harold, 211 E. Freedley St., Norristown, Pa.  
 Copeland, C. Willard, Remington Arms Co., Eddystone, Pa.  
 Cotton, G. W., Anaconda, Mont.  
 Cummings, W. L., Lansdowne, Pa.  
 Dabney, R. C., 119 Bassett Court, Lexington, Ky.  
 Davis, H. A., L. & N. Shops, So. Louisville, Ky.  
 Deacon, Frederick Sidney, 241 So. Melville St., Philadelphia, Pa.  
 De Eds, Floyd, 8925 Cedar Ave., Cleveland, Ohio.  
 Diercks, Henry C., 129 College Ave., Ithaca, N. Y.  
 Dixon, William V., Warner, N. Y.  
 Dorr, J. M., 17 Battery Place, New York City.  
 Doyle, Edgar J., 600 E. Fayette St., Syracuse, N. Y.  
 Dunham, Louis William, 124 So. 12th St., Newark, N. J.  
 Duval, Alexander L., 32 S. Wade Ave., Washington, Pa.  
 Eakins, E. E., cr Chas. Warner Lime Co., Devault, Pa.  
 Edgar, Graham, University, Va.  
 Eldred, Fred H., Y. M. C. A., Washington, D. C.  
 Elmer, Roy C., 111 Salem St., Woburn, Mass.  
 Ewing, Dr. John T., 308 W. Breckenridge, Louisville, Ky.  
 Eyssell, H. O., 3364 Gillham Rd., Kansas City, Mo.  
 Felt, Winchester W., 1340 Schilling Ave., Chicago Heights, Ill.  
 Field, Burnham E., 87 Gainsboro St., Boston, Mass.  
 Flagg, Frederick P., 20 Floyd St., Waltham, Mass.  
 Foltz, Edwin Chester, 447 Garden St., Louisville, Ky.  
 Ford, Miss Florence Marion, 1828 H St., Washington, D. C.  
 Foster, S. Lorraine, 1204 Jefferson St., Wilmington, Del.  
 Freyermuth, J. W., 304 So. Michigan St., South Bend, Ind.  
 Frick, Carl E., 617 Carroll St., Akron, Ohio.  
 Gamble, Miss Isabella A., 1024 S. 8th St., Terre Haute, Ind.  
 Gardner, J. Ellridge, 77 Mill St., South Weymouth, Mass.  
 Garrett, J. F., 54th St. & 1st Ave., Brooklyn, N. Y.  
 Garrod, Fred B., cr Owens Bottle Machine Co., Libby St., Toledo,  
 Ohio.  
 Gillam, John B., Coffeyville, Kans.  
 Gladding, Ernest K., cr du Pont Co., City Point, Va.  
 Goetz, Alvin C., 100 Division St., Amsterdam, N. Y.  
 Gore, John, 34 Rowe St., Auburndale, Mass.  
 Gosrow, Rolfe C., Heroult, Calif.  
 Hajek, William Jennings, 1231 So. Millard Ave., Chicago, Ill.  
 Hale, George C., 213 East Kirkwood Ave., Bloomington, Ind.  
 Hancher, Kenneth G., East Lansing, Mich.  
 Harding, Raymond B., South Euclid, Ohio.  
 Harger, Rollo N., 1428 Tennessee St., Lawrence, Kans.

Harvitt, Adolph, 192 Hooper St., Brooklyn, N. Y.  
 Hast, Julian J., 1512 Beechwood Blvd., Pittsburgh, Pa.  
 Hawks, Joseph Wm., 116 Hyland Ave., Ames, Iowa.  
 Hayes, Anson, 1012 Clark Ave., Ames, Iowa.  
 Heilbrunn, L. V., Zoology Bldg., University of Chicago, Chicago, Ill.  
 Helseth, S. T., 111 York St., Rumford, Maine.  
 Henderson, John C., 906 S. 6th St., Champaign, Ill.  
 Hibschman, Allen E., 677 Western Ave., Lynn, Mass.  
 Hickman, Reginald E., C. 56 Myrtle Ave., Irvington, N. J.  
 Hill, Harry H., U. S. Bureau of Mines, Pittsburgh, Pa.  
 Ho, Ching Tsang, 236 So. Thayer St., Ann Arbor, Mich.  
 Hocker, Carl DeWitt, 419 W. 115th St., New York City.  
 Hoke, Clarence Ballew, Chapel Hill, N. C.  
 Howard, J. W., Univ. of Mont., Missoula, Mont.  
 Howe, Harrison E., 93 Broad St., Boston, Mass.  
 Hughes, Eugene M., Fellows, Calif.  
 Hunt, W. C., cr. Hercules Powder Co., Carthage, Mo.  
 Hurwitz, Nathaniel, 526 Green St., Phila., Pa.  
 Hutchison, George F., 244 Millvale Ave., Pittsburgh, Pa.  
 Infield, C. H., 839 Monmouth St., Gloucester, N. J.  
 Jensen, John Henry, Aurora College, Aurora, Ill.  
 Johansen, Ernst, 500 Corinthian Ave., Philadelphia, Pa.  
 Johnson, Clare P., 200 West 72nd St., New York City.  
 Johnson, Robert E., 94 Randolph Ave., Waterbury, Conn.  
 Jones, Geo. W., 338 Main St., Pittsburgh, Pa.  
 Jurrissen, Dr. A. W., Martinez, Calif., cr. Shell Co. of Calif.  
 Kapkewich, Arthur, 25 Adams St., Kingston, N. Y.  
 Kauffman, M. H., Durango, Calif.  
 Kempter, Edward, 406 Avery Ave., Syracuse, N. Y.  
 Kenney, John A., 25 Sandford Ave., Plainfield, N. J.  
 Kimball, Herbert S., 111 Devonshire St., Boston, Mass.  
 Kirk, Raymond E., Chem. Dept., Iowa State College, Ames, Iowa.  
 Kinney, S. P., 1605 Walker Bank Bldg., Salt Lake City, Utah.  
 Kneeland, M. C., 5650 Aylesboro Ave., Pittsburgh, Pa.  
 Knudsen, Chas. W., Eureka, Ill.  
 Kraeger, J. F., 133 So. Ritter Ave., Indianapolis, Ind.  
 Kuzell, Charles R., cr. Washoe Reduction Works, Anaconda, Mont.  
 Lafferty, William R., General Chemical Co., Camden, N. J.  
 Landstrom, A. W., 917 W. Green St., Urbana, Ill.  
 Lange, N. A., 114 N. Ingalls St., Ann Arbor, Mich.  
 Laughlin, Jr., Homer, 602 Laughlin Bldg., Los Angeles, Calif.  
 Lavery, A. Leo, 229 Colchester Ave., Burlington, Vt.  
 Lenzing, Chester W., 917 W. Green St., Urbana, Ill.  
 Levitt, Benjamin, Swift & Co., Soap Works, East Cambridge, Mass.  
 Lewis, William E., 27 N. 15th St., Allentown, Pa.  
 Lichtin, James J., 3435 Webster Ave., Pittsburgh, Pa.  
 Loeb, Louis S., Lincoln Court, Meriden, Conn.  
 Loomis, John H., 11 Grey Court, Ithaca, N. Y.  
 Lorenz, Alfred D., 41 Williams Ave., Jersey City, N. J.  
 Lort, Alfred B., Bureau of Standards, Washington, D. C.  
 Loud, Irving B., 60 Bedford St., Stamford, Conn.  
 Loudermill, Joseph J., Vincennes Univ., Vincennes, Ind.

Luedeking, Carl C., 6143 Kingsbury Blvd., St. Louis, Mo.  
 MacLeod, Grace, 177 Emerson Place, Brooklyn, N. Y.  
 MacMillan, James A., 235 Byron St., Camden, N. J.  
 Macy, Philip A., 220 Elm St., W. Somerville, Mass.  
 McAuley, Auley, 1614 Kentucky St., Lawrence, Kans.  
 McDowall, C. D., cr. Lakeland Phos. Co., Lakeland, Fla.  
 McClure, S. M., 2029 Maple Ave., Evanston, Ill.  
 McLaughlin, H. M., Iowa State College, Ames, Iowa.  
 McMaster, L. D., 223 Helen St., Flint, Mich.  
 McMiller, P. R., Agri. Expt. Sta., St. Paul, Minn.  
 Mechling, D. G., 1049 5th St., Port Arthur, Tex.  
 Melick, John W., Toledo Rex Spray Co., Toledo, Ohio.  
 Mereness, Harry A., Riverside Club, Pennsgrove, N. J.  
 Merkle, Fred G., R 3, Box 8, Amherst, Mass.  
 Meyer, Edwin A., 69 East 120th St., New York City.  
 Miller, Marshall, 911 N. 8th St., Philadelphia, Pa.  
 Monroe, David W., P. O. 923, Falls St. Station, Niagara Falls, N. Y.  
 Moore, Virgil A., 317 Westfield Ave., Elizabeth, N. J.  
 Morgan, Mrs. Agnes Fay, cr. Univ. of Calif., Berkeley, Calif.  
 Morgan, Thurlow W., West Sixth St., Aspinwall, Pa.  
 Morris, F. J., cr. Dr. H. D. Morris, Port Arthur, Texas.  
 Moulton, Stanley C., 301 Market St., Charlottesville, Va.  
 Mumford, Russell W., 35 St. Nicholas Terrace, New York City.  
 Munch, Clyde, 609 S. Claytar Ave., Bloomington, Ill.  
 Newman, Joseph J., 4812 Indiana Ave., Chicago, Ill.  
 Newton, Grover C., Marionville, Mo.  
 Nixon, A. B., Hercules Club, Kenvil, N. J.  
 North, Dexter, 211 Newbury St., Boston, Mass.  
 Norton, Raymond P., 181 N. St., N. W., Washington, D. C.  
 Ohleen, Hadar P., 533 Stillwell Blvd., Port Arthur, Texas.  
 Osborn, J. B., Fidelity Cotton Oil Co., Houston, Tex.  
 Owen, C. W., 427 S. Upper St., Lexington, Ky.  
 Padgett, Fred W., Mellon Inst., Pittsburgh, Pa.  
 Park, Morey A., Parkesburg, Chester Co., Pa.  
 Parker, Clarence D., 16 Loring St., Lowell, Mass.  
 Parker, John Clinton, Pennsylvania Bldg., Philadelphia, Pa.  
 Pate, Wm. R., Box 382, University, Va.  
 Perkins, M. F., 3720 So. Yakima St., Tacoma, Wash.  
 Perey, R. A., 4953 Fountain Ave., St. Louis, Mo.  
 Perry, Margaret C., 108 N. Romine St., Urbana, Ill.  
 Pickering, Sam. E., 710 East Ave., Elyria, Ohio.  
 Porter, C. W., Logan, Utah.  
 Pruden, James Earl, cr. Procter & Gamble Co., Hamilton, Ont., Can.  
 Puddicombe, Sydney J., Oakdale, Pa.  
 Rabinovitz, Louis, 70 Greenwood Ave., Montclair, N. J.  
 Reed, James C., 43 West North St., Wilkes-Barre, Pa.  
 Reed, Robert F., 2836 Linwood Rd., Cincinnati, Ohio.  
 Reichel, Frank H., Saegertown, Pa.  
 Reichhard, Leonard G., 434 Central Park West, New York City.  
 Rogers, Hunton, 1318 Bolton St., Baltimore, Md.  
 Rogers, Morgan F., 75 Liberty Place, Weehawken, N. J.  
 Rohrs, Frank A., cr. Aetna Explosives Co. Inc., Fayville, Ill.



- Rothstein, Benjamin, 227 So. Second St., Brooklyn, N. Y.  
 Salls, C. M., 382 North St., Burlington, Vt.  
 Santosuosso, Nicholas, Norwich Univ., Northfield, Vt.  
 Sawyer, Joseph W., 2 Thompson St., Poughkeepsie, N. Y.  
 Schaefer, August, 586 Northrup St., Portland, Oregon.  
 Shaeffer, Ray, Box 128, New Comerstown, Ohio.  
 Schad, Fred, 197 Midwood St., Brooklyn, N. Y.  
 Schmidt, William G., 2815 N. 25th St., Philadelphia, Pa.  
 Scholler, F. C., 3301 North Amber St., Philadelphia, Pa.  
 Shonle, Horace R., 811 West Ill. St., Urbana, Ill.  
 Schuyler, William H., Bucknell Univ., Lewisburg, Pa.  
 Schultze, Wm., 31 Gerry Ave., Elmhurst, L. I., N. Y.  
 Schwartz, H. A., 2354 East 61st St., Cleveland, Ohio.  
 Schwarzwald, F. R., D. K. E. House, Middlebury College, Vt.  
 Scullen, Daniel V., 181 Main St., Cohoes, N. Y.  
 Seymour, Richard D., 314 South 52nd St., Philadelphia, Pa.  
 Shafran, Max J., cr. Atlas Powder Co., Tamaqua, Pa.  
 Simpkins, L. Duane, 2796 Dunkeld Place, Denver, Colo.  
 Smith, Julian F., 603 E. Stoughton St., Champaign, Ill.  
 Snider, John Blaine, cr. U. S. Assay Office, New York City.  
 Snyder, C. F., Box 488, Port Arthur, Texas.  
 Sokoloff, A. N., 751 Greene Ave., Brooklyn, N. Y.  
 Stambler, Benj., 1209 N. 7th St., Philadelphia, Pa.  
 Steinberg, Robert Aaron, 11 Lochinvar Apts., Norfolk, Va.  
 Stimson, Fred S., Newark, Ohio.  
 Stull, W. V., 22 Elizabeth Ave., Ferguson, Mo.  
 Sturgeon, Harry Elwyn, 215 Waldron St., W. Lafayette, Ind.  
 Tanke, C. E., 2310 Broadway, Indianapolis, Ind.  
 Thomas, O. L., 911 Adams St., Wilmington, Del.  
 Thornton, Henry C., 11 Woodland Ave., Stamford, Conn.  
 Tilton, W. J., 206 E. Green St., Champaign, Ill.  
 Town, Cecil B., Phi Delta House, Tufts College, Mass.  
 Trueblood, C. R., 2037 N. New Jersey St., Indianapolis, Ind.  
 Tucker, E. C., Y. M. C. A. Bldg., Holyoke, Mass.  
 Ullman, Paul, 125 Worth St., New York City.  
 Underhill, Frank P., 445 Orange St., New Haven, Conn.  
 Underwood, J. E., 241 McKee Place, Pittsburgh, Pa.  
 Van Arnam, Wm. D., 515 Stewart Ave., Ithaca, N. Y.  
 Van der Linden, Bernard Hugo, University Club, San Francisco, Calif.  
 Van Valkenburgh, H. B., Brownwood, Texas.  
 Van Zoeren, Gerrit John, MacDonald College, Quebec, Canada.  
 Vollmer, David Wilbert, 614 West 113th St., New York City.  
 Vollweiler, E. H., 917 W. Green St., Urbana, Ill.  
 Wagner, Richard, Jr., 160 Claremont Ave., New York City.  
 Waldron, William R., 125 Catharine St., Ithaca, N. Y.  
 Walker, Louis A., 201 Carver St., Warren, Pa.  
 Walker, Thaddeus, cr. Librarian, Wayne Co. Medical Society, 33 High St., Detroit, Mich.  
 Weber, Robt. R., B. P. Clapp Ammonia Co., Cincinnati, Ohio.  
 Webster, Paul F., 89 Bedford Ave., Buffalo, N. Y.  
 Weeks, Walter Seelye, Sigma Phi Place, Burlington, Vt.  
 Whitney, H. W., 603 The Arcade, Cleveland, Ohio.

Wilkins, Richard A., 97 St. Paul St., Brookline, Mass.  
 Wilson, Carl H., 9608 Hough Ave., Cleveland, Ohio.  
 Wilson, Herbert B., 15 Mason St., Rochester, N. Y.  
 Winkelstein, Abraham H., Massena, N. Y.  
 Wiswall, Charles L., Hercules Club House, Kenil, N. J.  
 Wong, Kei Tit, 127 N. State St., Ann Arbor, Mich.  
 Wood, A. E., Florence, Ala.  
 Wright, Harford H., 133 Peterborough St., Boston, Mass.  
 Zelle, Carl A., 501 E. Daniel St., Champaign, Ill.  
 Zoole, Leonard, Chemical Laboratory, Navy Yard, Philadelphia, Pa.

#### CORPORATION MEMBER.

Stresen-Reuter & Hancock, Inc., 1501 So. Peoria St., Chicago, Ill.

### MEETINGS OF THE SECTIONS.

[Full accounts of all meetings should be sent to Secretary Charles L. Parsons, Box 505, Washington, D. C.]

#### EASTERN NEW YORK SECTION.

The 61st meeting was held December 30th. The subject for the meeting was "Disposal of Municipal Waste in Schenectady." Papers were presented, as follows: "Garbage Reduction," by Mr. W. W. Chadsey, Deputy Commissioner of Public Works; "Treatment of Sewage," by Mr. W. E. Weller, Deputy City Engineer. The following officers were elected for the ensuing year: *President*, W. C. Arsem; *Vice-President*, M. A. Hunter; *Secretary-Treasurer*, A. J. Salathe; *Councilor*, W. D. Coolidge; *Advisory Committee*, Dr. E. Ellery, Dr. G. R. Fonda, Dr. S. Dushman.

W. E. RUDER, *Secretary*.

#### CINCINNATI SECTION.

The Cincinnati Section of the American Chemical Society celebrated its Twenty-Fifth Anniversary on the evenings of December the twentieth and twenty-first. Dr. Thomas H. Norton gave an illustrated lecture on "The Trend of American Technical Chemistry."

The 202nd regular meeting was held January 12th. Dr. W. H. Frost gave an illustrated lecture entitled: "An Outline of Studies by the U. S. Public Health Service on the Pollution of the Ohio River."

E. K. FLEIS, *Secretary*.

#### INDIANA SECTION.

The regular meeting was held January 14th. Program: "Commercial Applications of Oxygen," by Mr. Philip J. Kroll.

H. W. RHODEMANTEL, *Secretary*.

#### WASHINGTON SECTION.

The Annual Meeting was held January 13th. Program: Address of President Alsberg, on "The Chemical Analysis of Animal Nutri-

tion." The following were elected officers of the local Section of the American Chemical Society for the year 1916: *President*, R. B. Sosman, of the Geophysical Laboratory; *First Vice-President*, H. M. Loomis, of the Bureau of Chemistry; *Second Vice-President*, A. Seidell, of the Hygienic Laboratory; *Secretary*, E. C. McKelvy, of the Bureau of Standards; *Treasurer*, F. P. Dewey, of the Bureau of Mint; *Councilors*, J. Johnston, of the Geophysical Laboratory; R. C. Wells, of the Geological Survey; C. S. Hudson, of the Bureau of Chemistry; *Executive Committee*, J. C. Hostetter, of the Geophysical Laboratory; E. C. Schorey, of the Bureau of Soils; A. N. Finn, of the Bureau of Standards; M. J. Ingle, of the Bureau of Chemistry.

E. C. MCKELVY, *Secretary*.

#### ROCHESTER SECTION.

The regular meeting was held December 20th. Dr. W. F. Rittman from the Bureau of Mines of the Dept. of the Interior, Pittsburgh, Pa., gave a talk on "Thermal Reactions among Hydrocarbons in a Single Phase System."

A meeting was held January 3rd. Mr. F. R. Baxter gave a talk on "Oils."

The regular meeting was held January 17th. Mr. M. H. Eisenhart gave a talk on "The Manufacture of Acids."

H. H. TOZIER, *Secretary*.

#### CONNECTICUT VALLEY SECTION.

The 37th regular meeting was held January 8th. Program: "Our Experience with Nickel Anodes," by C. H. Corbin; "Some Experiments in Making Electrolytic Copper Pipe," by C. F. Wessell; "Mechanical Plating and Polishing," by G. B. Hoogaboom.

R. J. MARSH, *Secretary*.

#### PHILADELPHIA SECTION.

At a meeting held December 16th, the following officers were elected and installed for the coming year: *Chairman*, Mr. C. S. Brinton; *Vice-Chairman*, Mr. J. A. Branegan; *Secretary-Treasurer*, Mr. J. H. Graham; *Members of the Executive Committee*, Dr. G. D. Rosengarten, Mr. W. G. Bower, Mr. C. C. Tutweiler; *Councilors*, Dr. W. T. Taggart, Mr. J. S. Goldbaum, Mr. G. E. Barton, Mr. E. F. Hicks.

C. S. BRINTON, *Secretary*.

#### PITTSBURGH SECTION.

The 122nd regular meeting was held December 16th. The following officers were elected for the year 1916: *Chairman*, K. F. Stahl; *Vice-Chairman*, C. H. Viol; *Secretary*, W. C. Cope; *Treasurer*, C. E. Nesbitt; *Councilors*, F. C. Phillips, R. F. Bacon, and A. C. Fieldner. Program: "The Hydrometallurgy of Copper," by Raymond F. Bacon; "The Removal of Iron from a Municipal Water Supply," by S. Buka.

W. C. COPE, *Secretary*.

## UNIVERSITY OF MISSOURI SECTION.

The 63rd meeting and annual election of officers was held December 16th. The following officers were elected: *President*, J. W. Marden; *Vice-President*, Miss L. Stanley; *Treasurer*, E. E. Vanatta; *Secretary*, H. L. Dahm; *Councilor*, H. Schlundt.

H. L. DAHM, *Secretary*.

## SOUTHERN CALIFORNIA SECTION.

The annual meeting was held December 16th. The following officers were elected for 1916: *President*, Erwin H. Miller; *Vice-President*, Elbert E. Chandler; *Secretary*, Henry L. Payne; *Treasurer*, John S. Carman; *Councilor*, Edgar S. Baruch. Program: "The Manufacture of the Illuminating Mantle," by M. N. Lando.

H. L. PAYNE, *Secretary*.

## AMES SECTION.

The third regular meeting was held January 20th. Program: "Compounds of Ammonia and Certain Metallic Salts," by Dr. G. J. Fink; "Is the Hydrochloric Acid of the Gastric Juice Efficient as a Germicide?" by Dr. C. C. Fowler.

W. G. GAEBLER, *Secretary*.

## COLUMBUS SECTION:

A joint meeting of the Columbus Section of the American Chemical Society and Section "C" of the American Association for the Advancement of Science was held December 31st. Program: "Some Interesting Physical and Chemical Properties of Clays" (illustrated by experiments), by Arthur S. Watts; "The Contributions of Chemistry to the Production and Preparation of Human Food," by John F. Lyman; "The American Chemist and the War's Problems," by James R. Withrow; "The Fertilizer Resources of the United States," by Frank K. Cameron, Washington, D. C.

WM. J. McCAGHEY, *Secretary*.

## ST. LOUIS SECTION.

A special meeting of the section was held on Monday evening, December 6th. Dr. Walter F. Rittman, of the United States Bureau of Mines, addressed the section on "The Gasoline Situation in America."

The annual meeting was held December 13th, at the American Hotel. The officers for 1916 were elected as follows: *Chairman*, Mr. A. C. Boylston; *Vice-Chairman*, Mr. Gaston DuBois; *Secretary*, Geo. Lang, Jr.; *Treasurer*, Mr. J. D. Robertson; *Councilor*, Dr. L. McMaster. Mr. Boylston presented a paper on "Some Relations Between Chemical Constitution and Physiological Action."

A meeting was held Monday, January 10th. Program: Dr. F. O. Anderegg, of the Mallinckrodt Chemical Works, presented a paper on "The Silver Coulometer."

GEO. LANG, JR., *Secretary*.

## VIRGINIA SECTION.

The annual meeting of the section was held Friday, January 14th. Program: Dr. Frank R. Elder read a paper on "Tannin." Dr. F. B. Carpenter reviewed the potash situation. Mr. A. M. Förrester discussed the sulfuric acid situation.

W. A. BURROWS, *Secretary*.

## NASHVILLE SECTION.

The 37th meeting was held January 21st. Program: "The Simultaneous Developing and Fixing of Photographic Plates," by Dr. James F. Norris.

VICTOR P. LEE, *Secretary*.

## CLEVELAND SECTION.

The January meeting was held January 10th. Professor M. F. Coolbaugh spoke on "Experiments on the Electrolysis of Cyanide Solutions."

A. F. O. GERMANN, *Secretary*.

## LEXINGTON SECTION.

The 29th regular meeting was held January 13th. Program: "Report on the Annual Convention of the Association of Official Agricultural Chemists, for 1915," by Wm. Rodes, Jr.; "Note on a Specimen of Ferric Phosphate from Laurel County, Kentucky," by Dr. A. M. Peter; "Chemical Changes Occurring during the Ripening of the Wild Goose Plum," by J. S. McHargue.

P. L. BLUMENTHAL, *Secretary*.

## WISCONSIN SECTION.

The January meeting was held January 12th. Professor A. S. Loevenhart spoke on "Some Experiments on Animal Oxidations."

L. F. AUGSPURGER, *Secretary*.

## NEW YORK SECTION.

In the January Proceedings (p. 17, under this section) it should have read, "in conjunction with the New York Sections of the Society of Chemical Industry and the American Electrochemical Society."

## MILWAUKEE SECTION.

At the meeting of the section on December 24th, the following officers were elected for the ensuing year: *Chairman*, R. N. Bauer; *Vice-Chairman*, C. B. Rickey; *Secretary*, H. T. McAllister; *Treasurer*, F. L. Theurer; *Councilor*, A. J. Schedler.

GEORGE N. PRENTISS, *Chairman*.

## KANSAS CITY SECTION.

Officers elected at the December 11th meeting: *President (Chairman)*, Dr. W. A. Whitaker; *Vice-President*, C. S. Curtis; *Councilor*, E. H. S.

Bailey; *Secretary-Treasurer*, W. B. Smith; *Assistant Secretary*, G. W. Stratton.

W. B. SMITH *Secretary*.

DECEASED.

Robert J. Davidson, Blacksburg, Va., December 19, 1915.

Loran O. Potterf, Urbana, Ill., December, 1915.

# Proceedings.

## COUNCIL.

The Committee appointed in accordance with the resolution passed at the Seattle meeting to investigate the so-called "Westfield Campaign" and Lewis B. Allyn's connection therewith, as announced in the October, 1915, Proceedings, has been modified to consist of the following: Julius Stieglitz, *Chairman*; E. H. S. Bailey, A. D. Thorburn, L. P. Brown, L. W. Jones.

On January 12th the following communication was sent to the Council:  
COUNCILORS OF THE AMERICAN CHEMICAL SOCIETY.

GENTLEMEN:

At the Cincinnati meeting of the Council of the American Chemical Society the following paragraph was spread on the minutes:

"A communication was presented to the Council from the Secretary of the Committee on Organization and Membership of the American Association for the Advancement of Science, stating that the American Association had arranged to have, every four years, a meeting in one of our larger cities in the hopes that the American Chemical Society and other societies not now regularly affiliated with the Association might be induced to meet with them at these four-year periods. It was voted that the Secretary be instructed to reply that the sentiment of the Council was entirely favorable to the proposed plan, and to state that it is the opinion of the Council that the American Chemical Society will hold its annual meeting in 1916 with the American Association for the Advancement of Science at the place selected, convocation week, December-January, 1916-1917."

At the Seattle meeting of the Council the following paragraph was spread on the minutes:

"The Council voted that time and place of the Fall meeting for 1916 be left to the President and Secretary with the understanding that as soon as the constitutional limit of one year previous to the date of the meeting had been reached, the President and Secretary would announce New York as the place of the meeting as per previous understanding that the meeting should be held in affiliation with the American Association for the Advancement of Science."

When the vote was passed at Seattle it was understood that the second National Exposition of Chemical Industries would be held in New York City during the last week of December, 1916. Since that time, however, the Exposition authorities have found it impossible to do so, owing to the fact that the Grand Central Palace has been engaged for the 1916-1917

automobile show at that time. They were, accordingly, obliged, such to their regret, to change the date of their Exposition to the week beginning Monday, September 25, 1916.

The success of the first National Exposition of Chemical Industries is well known to the Council. It seems certain that there will be a large gathering of chemists on account of this Exposition in New York City in the week beginning September 25, 1916, and that many of our members would not wish to come twice to New York during the Fall of this year. The second National Exposition of Chemical Industries promises to be one of the most successful expositions ever held in this country having any bearing on our chemical activities. This seems doubly certain on account of the great opportunities for our chemical industries arising from commercial conditions depending on the foreign situation.

I have just received from President Herty the invitation of the New York Section inviting the American Chemical Society to hold its annual meeting in the City of New York during the week beginning September 25, 1916, on account of the fact that the second National Exposition of Chemical Industries is to be held at that time. I have no doubt that, if the Council deem it advisable, the New York Section will amend this invitation to make their date coincide with that of the meeting of the Association for the Advancement of Science.

For your information, I would state that rooms for the meeting of the Society are available either in September or December.

Under the above conditions, the President and Secretary do not feel that the decision should lie with them, and this communication is therefore sent to you in the form of a letter ballot. Kindly indicate your preference below.

Yours very truly,

CHARLES L. PARSONS,  
*Secretary.*

Mark your choice with an X.

1. In favor of having the annual meeting for 1916 in New York City in the week beginning September 25, 1916.

2. In favor of having the annual meeting of the American Chemical Society in New York City in the week beginning December 25, 1916.

On February 3rd the vote was counted by Messrs. F. G. Cottrell, Chas. L. Parsons and J. D. Davis, Committee, and the result was as follows; in favor of September 25th date, 54; in favor of December 25th date, 30; illegal ballots 4. Accordingly, the invitation of the New York Section to hold the Fall meeting of 1916 in New York City on September 25th was accepted and a communication to this effect was transmitted to the chairman of the Section.



## MEMBERS ELECTED BETWEEN JANUARY 15 AND FEBRUARY 15, 1916.

- Baeza, Walter J., 839 West End Ave., New York City.  
 Bailey, R. K., Cliffside, Texas.  
 Baird, Madeline, 1135 Fourth St., Portsmouth, Ohio.  
 Baker, Fred P., 906 S. Sixth St., Champaign, Ill.  
 Barker, H. H., 1361 Logan St., Denver, Colo.  
 Bechtel, F. Clarke, Phi Sigma Kappa House, State College, Pa.  
 Beckerman, Harry, 2019 South Sixth St., Philadelphia, Pa.  
 Beebe, Morris W., 131 College Place, Syracuse, N. Y.  
 Bennett, Otto R., Jr., Manchester, Vt.  
 Bethea, Andrew Jackson, 234 Park Ave., West, Mansfield, Ohio.  
 Beverly, F. F., 1229 University Avenue, Boulder, Colo.  
 Bivins, Chalfant E., 179 Steuben St., Brooklyn, N. Y.  
 Bluhm, Harold J., 404 E. Chalmers St., Champaign, Ill.  
 Boutwell, Paul W., 708 W. Dayton St., Madison, Wisc.  
 Branch, G. E. K., Dept. of Chemistry, Univ. of California, Berkeley, Calif.  
 Brooke, H. Carroll, Westmoreland and C Sts., Philadelphia, Pa.  
 Brownell, Kenneth A., 700 Main St., Pawtucket, R. I.  
 Buchwald, Charles, Experiment Station, College Station, Texas.  
 Burns, Joseph F., P. O. 1336, Miami, Ariz.  
 Butterman, Samuel, 1536 So. Millard Ave., Chicago, Ill.  
 Campbell, David E., 358 Barclay St., Burlington, N. J.  
 Campbell, Robert W., 199 Meade St., Wilkinsburg, Pa.  
 Carpenter, Henry A., Leetsdale, Pa.  
 Case, F. O., 505 Dryden Rd., Ithaca, N. Y.  
 Case, John H., 921 Fifth Ave., N., Great Falls, Mont.  
 Champney, Hubert H., c/o Union Powder Corp., Parlin, N. J.  
 Chiles, Howard M., 205 E. Armory Ave., Champaign, Ill.  
 Clark, Norman, 420 West 119th St., New York City.  
 Clark, Willis H., 145 W. Hancock Ave., Detroit, Mich.  
 Clement, Marwood R., 178 Willoughby Ave., Brooklyn, N. Y.  
 Clover, Dr. A. M., c/o Parke Davis & Co., Detroit, Mich.  
 Cohen, William B., 48 Broome St., New York City.  
 Coleman, Thomas H., 1200 So. Evans Ave., McKeesport, Pa.  
 Cooley, Lloyd C., 75 Pitts St., Boston, Mass.  
 Corbett, Edwin E., 181 Lincoln Rd., Brooklyn, N. Y.  
 Culmer, Thaddeus W., 415 Broadway St., Vincennes, Ind.  
 Dewar, Robert, 48 E. Stewart Ave., Lansdowne, Pa.  
 Drucker, Samuel, 616 E. 46 St., Chicago, Ill.  
 Duncombe, Chas. G., 2149 $\frac{1}{2}$  N. High St., Columbus, Ohio.  
 Durfee, Earl, c/o Toledo Sugar Co., Toledo, Ohio.  
 Eckstein, Henry C., 1003 W. Illinois St., Urbana, Ill.  
 Elias, Nathan M., 423 E. 158 St., New York City.  
 Ellefson, Elven T., 2600 Bancroft Way, Berkeley, Calif.  
 Engerud, Louis, c/o Patterson-Sargent Co., Cleveland, Ohio.  
 Fabre, E., 125 Columbus St., Elyria, Ohio.  
 Fancourt, W. F., 516 So. Delaware Ave., Philadelphia, Pa.  
 Faville, Katharine, 419 Sterling Place, Madison, Wisc.  
 Fernandez, Candido, Norte Dame, Indiana.  
 Finkl, Wm. F., 5214 Lakewood Ave., Chicago, Ill.

- Ford, Jay T., Box 107, Chem. Bldg., Univ. of Illinois, Urbana, Ill.  
 Frazier, J. I., 93 East Cedar St., St. Charles, Ill.  
 Frear, Clyde L., School of Mining, Kingston, Ontario, Canada.  
 Frisbie, Raymond L., Joliet, Ill.  
 Geiling, E. M. K., 407 E. Daniel, Champaign, Ill.  
 Gifford, M. S., La Porte, Ind.  
 Gould, David Foster, c/o General Lead Batteries Co., Chapel St. and  
 Listey Ave., Newark, N. J.  
 Hadfield, Wm. A., 212 E. Mifflin St., Madison, Wisc.  
 Haldenstein, Alfred Augustus, 321 West 92nd St., New York City.  
 Hamill, George K., 11 Congress St., Stoneham, Mass.  
 Harlow, L. C., Agricultural College, Truro, Nova Scotia, Canada.  
 Harnist, Milton J., 529 St. Louis St., Edwardsville, Ill.  
 Harvey, David, 24 Florence Ave., Norwood, Mass.  
 Harvey, Thos. R., Mellon Institute, Pittsburgh, Pa.  
 Hatfield, W. Durrell, State Water Survey, Urbana, Ill.  
 Hawthorne, N. G., Hercules, Calif.  
 Hemingway, E. Heaton, 51 Prospect St., New Haven, Conn.  
 Herzog, Carl, Dr., 1254 Arch St., Shamokin, Pa.  
 Heyne, H. R., Magnolia Petroleum Co., Beaumont, Texas.  
 Hill, J. Bennett, 409 N. 36th St., Philadelphia, Pa.  
 Hillmann, William P., 30 Duffield St., Brooklyn, N. Y.  
 Hodge, Willard W., 531 Ferry St., Albany, Ore.  
 Hooker, Elon Huntington, 40 Wall St., New York City.  
 Isenberg, Nathan, 1448 Washburne Ave., Chicago, Ill.  
 Jeffers, Roland H., Box 612, Coatesville, Pa.  
 Jenckes, Thomas A., Jr., 88 Prospect St., Providence, R. I.  
 Johns, John J., c/o Union Sulphur Co., Sulphur, La.  
 Jones, C. Heyburn, Riverside Club House, Pennsgrove, N. J.  
 Katz, Jr., Richard, 150 West 19th St., New York City.  
 Keith, M. Helen, University of Illinois, Urbana, Ill.  
 Kellems, T. O., 517 Welch Ave., Ames, Iowa.  
 Klonin, Oscar S., 5170 Columbia Ave., W. Philadelphia, Pa.  
 Knapp, Paul, 17 South Ave., Ithaca, N. Y.  
 Knowles, Wm. V., Titanium Alloy Mfg. Co., Niagara Falls, N. Y.  
 Kohr, A. Allison, 308 Meyran Ave., Oakland, Pittsburgh, Pa.  
 Kossler, Albert L., 1007 W. Illinois St., Urbana, Ill.  
 Kraus, Elmer C., 4430 Winton Rd., Cincinnati, Ohio.  
 Landis, Wilber C., 137 S. Atherton St., State College, Pa.  
 Lawrence, Neal B., 470 Hazelwood Ter., Rochester, N. Y.  
 Lemp, John F., 206 E. John St., Champaign, Ill.  
 Lentz, C. E., 1235 Lincolnway, West, South Bend, Ind.  
 Lewis, S. H., No. 4, James River Y. M. C. A., du Pont Powder Co.,  
 City Point, Va.  
 Lillian, Sister Marie, St. Clara College, Sinsinawa, Wisc.  
 Long, Barrin Y., 266 Oakland Ave., Pittsburgh, Pa.  
 Lorenz, Joseph R., 980 Eleventh St., Milwaukee, Wisc.  
 Love, Henry L., Bacchus, Utah.  
 Lowy, Benno, 952 Sutter St., San Francisco, Calif.  
 Luckow, William C., 534 East 46th Place, Chicago, Ill.  
 Manning, Eugene R., 1213 Gilpin Ave., Wilmington, Del.  
 Martenet, S. J., Acme, N. C.

Marx, Victor Emanuel, 1541 Birchwood Ave., Chicago, Ill.  
 Mason, Frederick Alfred, Dr., 21 Queen Sq., London, W. C., England.  
 Mayor, W. Waldo, 210 Greene Ave., Brooklyn, N. Y.  
 McCandlish, Andrew C., Animal Husbandry Dept., Ames, Iowa.  
 Meese, Fred A., Y. M. C. A., Gary, Ind.  
 Megraw, James C., Jr., 916 Twelfth Ave., Moores, Pa.  
 Micheuer, John H., 15 South Ave., Ithaca, N. Y.  
 Mills, William W., Midland, Pa.  
 Mitzen, Harry, 304 N. Carey St., Baltimore, Md.  
 Monsalvatge, R. F., Southern Cotton Oil Co., New Orleans, La.  
 Moore, Neil Preston, 564 Hamilton Ave., Palo Alto, Calif.  
 Moore, Robert Jerome, Department of Chemistry, Columbia University, New York City.  
 Mullikin, Richard N., Mellon Institute, Pittsburgh, Pa.  
 Murtagh, Edw., Jr., Municipal Bldg., Rochester, N. Y.  
 Nakamura, Tamiichi, c/o Mr. Birch, 204 Fifth St., Niagara Falls, N. Y.  
 O'Connell, Thos. C., c/o A. Z. & C. Co., Langeloth, Pa.  
 O'Kane, Robert Guy, Santiago de las Vegas, Cuba.  
 Oshima, Yoshikiyo, c/o Takata & Co., 50 Church St., New York City.  
 Palmer, Fred C., 24 Weston St., Burlington, Vt.  
 Perlstein, George B., 4930 Champlain Ave., Chicago, Ill.  
 Phillips, Ernest B., P. O. Box 174, Port Arthur, Texas.  
 Pierle, Chester A., Tsing Hua College, Peking, China.  
 Polakow, A. H., 1006 $\frac{1}{2}$  W. Green St., Urbana, Ill.  
 Powell, Sargent G., 1018 Thirty-seventh Ave., No., Seattle, Wash.  
 Quimby, Norman L., 109 Twelfth Ave., Juniata, Pa.  
 Ricketts, W. C., 1536 E. 94th St., Chicago, Ill.  
 Rigg, William L., Deloro Mining & Reduction Co., Ltd., Deloro, Ontario, Canada.  
 Ritter, C. Martin, 312 Fifth Ave., Carnegie, Pa.  
 Rivett, Byron J., 352 Whitney Ave., Detroit, Mich.  
 Roessler, Emil B., 3459 Brookline Ave., Cincinnati, Ohio.  
 Rogers, Harold Lee, Box 339, Massena, N. Y.  
 Ross, J. C., 407 Daniel St., Champaign, Ill.  
 Rosskam, Walter M., 13 Cleeman, Univ. of Penna. Dormitories, Philadelphia, Pa.  
 Ruger, M. Selden, 1004 Oakland Ave., Ann Arbor, Mich.  
 Sawyer, Geo. B., 2308 Murray Hill Rd., Cleveland, Ohio.  
 Schmid, Edward R., Ford Hall, New Brunswick, N. J.  
 Scott, Lester C., 976 St. Johns Place, Brooklyn, N. Y.  
 Seaman, Stewart E., 236 Lincoln Rd., Brooklyn, N. Y.  
 Segnitz, Paul Herman, 117 De Witt Place, Ithaca, N. Y.  
 Sharp, Leslis H., Stanford University, Calif.  
 Shoub, Hyman L., Hygienic Laboratory, Washington, D. C.  
 Slyhoff, R., 4735 Richmond St., Bridesburg, Philadelphia, Pa.  
 Spenceley, George W., Box 455, Dauphin, Manitoba, Canada.  
 Stanford, Forrest G., 1627 Winona Blvd., Los Angeles, Calif.  
 Starrels, Joel, 222 Riverside Drive, New York City.  
 Stearns, Harold C., Westport, Conn.  
 Stewart, Andrew H., 801 Hill Ave., Wilkinsburg, Pa.  
 Stewart, Olus J., Durham, N. H.

Stewart, T. Dale, 2600 Bancroft Way, Berkeley, Calif.  
 Strattner, Lawrence W., 127 N. Main St., Mechanicville, N. Y.  
 Tarr, Lester W., Experiment Station, Newark, Dela.  
 Tendick, F. H., 922 W. Illinois St., Urbana, Ill.  
 Toomer, J. E., Mascot, Tenn.  
 Townsen, J. Wilbur, Phi Delta Theta House, State College, Pa.  
 Tuchscher, Frank A., 619 Lake St., Madison, Wisc.  
 Untersee, Philip, 262 Ryerson St., Brooklyn, N. Y.  
 Updegraff, Helen, 1008 California St., Urbana, Ill.  
 Van Brocklin, F. Ray, 508 So. Albany St., Ithaca, N. Y.  
 Van Vleet, Cecil Spicer, Beswick, Calif.  
 Waffle, E. R., Iowa State College, Ames, Iowa.  
 Waite, Ralph B., Spencer, So. Dak.  
 Ward, L. Da Costa, 320 So. Broad St., Philadelphia, Pa.  
 Warner, E. Robert, 30 Oraton St., Newark, N. J.  
 Weatherill, Philip F., Brunswick, Maine.  
 Weiss, Morris, Harriman Research Laboratory, Roosevelt Hospital,  
 New York City.  
 Westhafer, T. O., R. 107 Chemistry Bldg., Univ. of Illinois, Urbana,  
 Ill.  
 White, Edwin C., 5812 Bartlett St., Pittsburgh, Pa.  
 Whittemore, Francis D., c/o du Pont Co., Lab., Haskell, N. J.  
 Wilkens, Henry B., 1925 N. Fairfield Ave., Chicago, Ill.  
 Williams, H. C., 29 Edgemont Ave., Summit, N. J.  
 Williamson, C. G., 14 Bradley St., Burlington, Vt.  
 Winship, William Winchester, c/o Thermal Syndicate Ltd., Chemists'  
 Bldg., New York City.

## MEETINGS OF THE SECTIONS.

[Full accounts of all meetings should be sent to Secretary Charles L. Parsons, Box 505,  
 Washington, D. C.]

### CALIFORNIA SECTION.

The eighty-eighth regular meeting was held January 22nd. Program:  
 "Electrochemical Possibilities of California as Compared with those of  
 Sweden and Norway," by J. W. Beckman. "Solutions of Metals in  
 Liquid Ammonia," by W. L. Argo.

BRYANT S. DRAKE, *Secretary*.

### NORTHERN INTERMOUNTAIN SECTION.

The Section held a meeting at Pullman, Washington, December 11th.  
 Program: "Notes on the Homedale Nitrate and Potash Deposits," by  
 Professor C. C. Todd. "The Effect of Dihydroxystearic Acid and  
 Uvitonic Acid in Soil and in Water Solution," by Professor P. P. Peterson.  
 "Gluten Formation in Wheat Kernel," by Professor George A. Olson.

GEO. A. OLSON, *Secretary*.

### LEXINGTON SECTION.

The Section held its 30th regular meeting February 10th. Program:  
 Review of Soil Nitrogen as a Measure of the Organic Matter in Soils,"  
 by S. D. [unclear]. Paper—"Variations in the Mineral Composition of the

Sap, Leaves and Stems of the Wild Grape Vine and the Sugar Maple Tree," by O. M. Shedd.

PHILIP L. BLUMENTHAL, *Secretary*.

#### INDIANA SECTION.

The January meeting was held January 14th. Mr. Philip J. Kroll gave an illustrated talk on the "Technical Application of Oxygen."

The February meeting was held February 11th. Program: "An Ex-Official's View of Food Control Work," by T. J. Bryan.

H. W. RHODENHAMEL, *Secretary*.

#### ST. LOUIS SECTION.

The Section met February 7th. Program: "The Practical Sterilization of Water as Affected by the War," by W. F. Monfort.

GEO. LANG, JR., *Secretary*.

#### PITTSBURGH SECTION.

The 123rd regular meeting was held January 20th. The paper of the evening was presented by Mr. Joseph E. Babb, Supt. Fort Pitt Oil & Paint Co. "Lubricating Greases: their Composition, and Methods of Analysis."

The 124th regular meeting was held February 17th. Program: "Thermal Reactions Among Hydrocarbons at High Temperatures," by W. F. Rittman, U. S. Bureau of Mines. "The Corrosive Resistance of Copper Steel," by D. M. Buck, Chemist American Sheet & Tin Plate Co., and J. O. Handy, Director Pittsburgh Testing Laboratories.

W. C. COPE, *Secretary*.

#### DETROIT SECTION.

The January meeting was held January 20th. Program: "Formaldehyzed Capsules," by Wilbur L. Scoville. "The Theory and Practice of Case Hardening," by Herman G. Kiefer.

EDWARD J. GUTSCH, *Secretary*.

#### VIRGINIA SECTION.

The February meeting was held February 11th. The following papers were read: "Some Research Problems," by Dr. J. B. Weems. "Sulfides in Flowers of Sulfur," by Mr. R. F. McCrackan, Mr. O. L. Barden and Mr. R. C. Courtney. "Chemical Methods for Differentiating Cotton, Wool and Silk," by Dr. E. C. L. Miller and Mr. J. C. Ford.

At the January meeting the following officers were elected: *President*, R. B. Arnold; *Vice-President*, Dr. E. C. L. Miller; *Secretary-Treasurer*, W. A. Burrows; *Councilor*, Dr. E. W. Magruder.

W. A. BURROWS, *Secretary*.

#### NEW HAVEN SECTION.

At the annual meeting on January 14th, the following officers were elected for 1916: Ralph G. Van Name, *President*; C. H. Matthewson, *Vice-President*; Wm. Druschel, *Treasurer*; T. B. Johnson, *Councilor*; G. S. Jamieson, *Secretary*.

G. S. JAMIESON, *Secretary*.

## OREGON SECTION.

The annual meeting of the Section was held November 27, 1916. The paper of the evening was by Wm. Conger Morgan on "Some Modern Views of Matter." The following were elected to serve as officers for 1916: Wm. Conger Morgan, *President*; O. F. Stafford, *Vice-President*; Norman C. Thorne, *Secretary*; H. V. Tartar, *Councilor*.

The 26th regular meeting was held February 5th. The paper of the evening, "The Synthesis of Metals," by A. A. Knowlton.

NORMAN C. THORNE, *Secretary*.

## GEORGIA SECTION.

The following have been elected to serve as officers of the Section for 1916: V. H. Bassett, *President*; T. C. Law, *Vice-President*; J. S. Brogdon, *Secretary*; F. N. Smalley, *Councilor*.

J. S. BROGDON, *Secretary*.

## RHODE ISLAND SECTION.

The regular meeting was held January 21st. Program: "Green Gills in Oysters," by Prof. P. H. Mitchell.

The February meeting was held February 18th. Program: "Sympathetic on Induced Reactions," by A. B. Lamb.

ROBT. F. CHAMBERS, *Secretary*.

## CHICAGO SECTION.

The regular meeting was held January 21st. Program: "The Chemistry of Glass Making," by Dr. Alexander Silverman.

D. K. FRENCH, *Secretary*.

## PHILADELPHIA SECTION.

The regular meeting was held January 20th. Program: An address on "The Extraction and Recovery of Radium, Uranium and Vanadium from Carnotite," by Charles L. Parsons.

J. HOWARD GRAHAM, *Secretary*.

## MINNESOTA SECTION.

The Section met January 21st. Dr. Ross A. Gortner spoke on "Animal Pigments," and Dr. J. F. McClendon spoke on "The Physiological and Biochemical Significance of Hydrogen Ion Concentration."

The Section met February 18th. F. W. Emmons spoke on "The Chemist and the Flour Industry," and E. K. Strachan spoke on "Nonideal Solutions."

STERLING TEMPLE, *Secretary*.

## PUGET SOUND SECTION.

The regular meeting was held January 29th. A paper on "Plasticity of Clays," illustrated by data, was presented by R. F. McMichael.

H. L. TRUMBULL, *Secretary*.

## UNIVERSITY OF MICHIGAN SECTION.

The January meeting was held Tuesday, January 25th. Mr. R. J. Carney gave a paper on "The Determination of Thorium in Monazite Sand."

H. H. WILLARD, *Secretary*.

#### CORNELL SECTION.

A research meeting was held January 25th. The following papers were presented: "The Electrolytic Production of Perchlorates," by E. L. Mack. "The Nitration Products of Phenoltetrachlorophthalein and Some of Its Derivatives," by J. J. Kennedy. "The Electrolysis of Solutions of the Rare Earths," by A. B. Ray. J. A. BRIDGMAN, *Secretary*.

#### UNIVERSITY OF ILLINOIS SECTION.

The regular meeting was held January 18th. Program: "Syntheses in the Naphthalene Series," by Mr. H. B. McCluggage and Dr. Oliver Kamm. "Triphenylmethyl," by Dr. Laurence C. Johnson.

The regular February meeting was held February 15th. Program: "Qualitative Tests for Drugs Containing Emodin," by Ruth E. Okey and G. D. Beal. "Preparation and Characterization of Trimethylene-oxide," by C. G. Derick and D. W. Bissell. "The Preparation of Conductivity Water," by E. W. Washburn and H. J. Weiland.

G. D. BEAL, *Secretary*.

#### KANSAS CITY SECTION.

The 114th regular meeting was held January 22nd. Program: "Vanadium." "The Metallurgy of Vanadium," by Mr. R. L. Grider. "The Chemistry of Vanadium," by Dr. P. V. Faragher. "Vanadium Steels," by Mr. Clarence Estes.

W. B. SMITH, *Secretary*.

#### ROCHESTER SECTION.

The regular meeting was held February 7th. Prof. Alexander Smith, of Columbia University, gave a talk on "Sulfur."

H. H. TOZIER, *Secretary*.

#### WISCONSIN SECTION.

The February meeting was held February 16th. Professor L. Kahlenberg spoke on "A Neglected Principle of Chemistry."

L. F. AUGSPURGER, *Secretary*.

#### CONNECTICUT VALLEY SECTION.

The 38th regular meeting was held February 12th. Program: "The Chemistry of Synthetic Caoutchouc," by Prof. Joseph S. Chamberlain. "The Color Problem in the Paper Industry," by Mr. R. F. Hatch.

R. J. MARSH, *Secretary*.

#### MARYLAND SECTION.

The 11th regular meeting was held February 12th. Program: "The Estimation of Sugar in the Blood," by Dr. Geo. Peirce of Johns Hopkins Hospital.

FRANK M. BOYLES, *Secretary*.

#### CLEVELAND SECTION.

Dr. Chas. H. Viol, Director of the Radium Research Laboratory of the Standard Chemical Company, Pittsburgh, addressed the Section February 14th on the subject: "Radium and Radio-Activity."

A. F. O. GERMANN, *Secretary*.

#### COLUMBUS SECTION.

The February meeting was held February 11th. Program: "Some Problems in Municipal Chemistry," by Mr. C. B. Hoover, Chemist in charge of Sewage Disposal, Columbus, Ohio. "The Present Chemical Situation as Related to Problems in Water Purification," by Mr. Charles P. Hoover, Chemist at The Municipal Filtration Plant, Columbus, Ohio.

W. J. McCaughey, *Secretary*.

#### WESTERN NEW YORK SECTION.

The regular meeting was held February 17th. "Manufacture and Bacteriology of Ice Cream," by H. F. Lichtenberg. R. H. White, *Secretary*.

#### DECEASED.

Stanley Feather Hodgson, Mellon Institute, Pittsburgh, died Jan. 7th.  
W. A. Langdon, 225 N. 4th St., Allentown, Pa., died Jan. 20th.

J. H. Payne, 4004 Dalrymple Ave., Baltimore, died Jan. 28th.

#### Sir Henry Roscoe.

The name of Roscoe has long been a household word among chemists. True, his activity in chemical lines came practically to an end about thirty years ago when he resigned his professorship and entered Parliament, but his text-books continued in extensive use and either "little Roscoe" or "Roscoe and Schorlemmer," or both, are known wherever the science of chemistry is cultivated.

The Rt. Hon. Sir Henry Enfield Roscoe died suddenly at his residence near London on December 18th. He had nearly completed his 83rd year, having been born January 7, 1833. He had always enjoyed good health except for occasional attacks of gout, and up to within an hour of his death he was well and happy. "Heart failure" is given as the cause of his ideal end.

Roscoe's grandfather, William Roscoe, rose to distinction, having represented Liverpool in Parliament in 1806. His "Lives of Lorenzo di Medici and Leo X" is well known and is his chief claim to fame. His son, Henry Roscoe, the father of Sir Henry, was a barrister who became a judge in Liverpool. He died at an early age and left his widow in straitened circumstances. She gave lessons in painting to help her to support her family. Later she published a "Life of Vittoria Colonna." She was a woman of unusual ability and force of character.

Roscoe's early education was obtained at the High School of Liverpool. His teacher in science was Balmain, the discoverer of luminous paint, and from him he acquired a taste for scientific studies. In his interesting "Life and Experiences," published in 1906, he tells us that at this early period of his life he attended a lecture by Mr. Pepper (of ghost fame). He says the thought passed through his mind: "Shall I ever attain to the



position of a scientific lecturer and burn phosphorus in oxygen on a large scale before an admiring audience?"

He was sent to University College, London, in 1848. Graham was then the professor of chemistry there, and he was succeeded by Williamson during Roscoe's student years, so that he had the good fortune to come under the influence of both of these able men. He received the degree of B.A. from the University of London. He then went to Heidelberg to continue his studies under Bunsen. Here he took part in the well-known researches on the chemical action of light. He continued work in this field for some years after receiving the degree of Doctor of Philosophy from Heidelberg in 1854, returning to Heidelberg in the summer vacations for this purpose. The results of the investigations were published in the *Philosophical Transactions* and in Poggendorff's *Annalen*. In Ostwald's reprint in his *Collection of Scientific Classics*, he says: "The Photo-Chemical researches of Bunsen and Roscoe deserve the name of a classical investigation as they not only have gathered together all points known hitherto on the subject, but by their wide and thorough experiments have laid the foundation for all further work on the subject. It cannot be doubted that these researches not only serve as a classical, but as *the* classical type for all future experiments on the subject of physical chemistry."

Roscoe's residence in Heidelberg and his association with Bunsen and with Kirchhoff naturally led him to take special interest in spectrum analysis. He translated the book of Bunsen and Kirchhoff and also lectured extensively on this subject.

In 1857 he was elected professor of chemistry in Owens College, Manchester, succeeding Frankland. The College had then been in existence only six years, and it was in a low state financially. In his "Life and Experiences" he says: "The institution was at that time nearly in a state of collapse, and this fact had impressed itself even on the professors. I was standing one evening, preparing myself for my lecture by smoking a cigar at the back gate of the building, when a tramp accosted me and asked me if this was the Manchester Night Asylum. I replied that it was not, but that if he would call again in six months he might find lodging there! That this opinion as to the future of the college was also generally prevalent is shown by the fact that the tenancy of a house in Dover Street was actually refused to me when the landlord learned that I was a professor in that institution."

His principal work was done while holding the professorship in Owens College, which he resigned in 1885 to enter Parliament, after a continuous service of 28 years. During this period the college became completely transformed and in 1880 a Royal Charter constituting the Victoria University was granted. Of this new university Owens College was a part,

the other parts being the University College of Liverpool and the Yorkshire College of Leeds.

There can be no doubt that Roscoe rendered his country a great service in improving the methods of teaching chemistry. In this work he was ably seconded by Carl Schorlemmer, a German who was thoroughly imbued with the spirit of the German universities. He held the chair of Organic Chemistry and distinguished himself by his researches and by his literary work. Roscoe had great admiration for the German methods and he did what he could to give his laboratory the advantage of these methods.

Roscoe's contributions to chemistry are not numerous. Probably the most important is that on vanadium. He says: "This is certainly the best piece of work I ever did and I do not know that I ever enjoyed anything of an intellectual kind more thoroughly." \* \* \* "The subject aroused very general attention throughout the scientific world, and my view concerning the relationships of the metal was universally adopted. Those who wish to understand this matter more fully can read the papers in the *Philosophical Transactions* (Bakerian Lecture, 1868), and also several lectures on the subject which I gave at the Royal Institution." \* \* \* "The explanation of the close resemblance between vanadium on the one hand, and phosphorus and arsenic on the other, is the chief outcome of this work."

His "Lessons in Elementary Chemistry" was published in 1866. Up to 1906 the number of copies sold was 211,000. Translations appeared in German, Russian, Italian, Hungarian, Polish, Swedish, Japanese, and even in one of the Indian vernaculars, Urdu. His *Primer* had also a wide, in fact, a still wider circulation. Up to 1906, 355,000 copies were sold. It was translated into Icelandic, Polish, German, Italian, Japanese, Bengali, Turkish, Malayalam, and Tamil!

The well-known "Treatise on Chemistry" by Roscoe and Schorlemmer is unquestionably the best English treatise in chemistry and certainly one of the best in any language. It was translated into German by Schorlemmer and published in 1880 by Vieweg.

As has already been stated Roscoe was elected to Parliament in 1885, and then resigned the professorship. Since that time his activities have not been displayed especially in the field of chemistry. He, however, continued to exert a strong influence upon educational matters. After his retirement from Parliament he and his wife lived in what he called "the most beautiful and healthy spot in the whole of Surrey, namely, at Woodcote Lodge." This is only twenty-six miles from Hyde Park Corner, but "as far from the madding crowd" as if it "were ten times that distance." It was here that Roscoe's useful life ended suddenly and ideally.

IRA REMSEN.

# Proceedings.

## COUNCIL.

March 2, 1916.

### COUNCIL OF THE AMERICAN CHEMICAL SOCIETY.

*Gentlemen:*

On February 14th a letter was received from Prof. W. A. Noyes moving reconsideration of the recent vote selecting the date of September 25, 1916, for the time of our Annual Meeting rather than Convocation Week in December. Under vote of the Council (*Proc.*, 1912, p. 43), it is necessary that the President certify to the urgency of this vote before it can be sent to the Council. After some correspondence between Professor Noyes and President Herty, I am this morning in receipt of a letter from President Herty certifying to the urgency of the matter, and Professor Noyes' motion to reconsider is accordingly submitted to you for your opinion. Professor Noyes' motion and President Herty's letter to me regarding the matter follow:

"February 10, 1916.

PROFESSOR C. L. PARSONS,

Washington, D. C.

*Dear Professor Parsons:*

In the recent vote of the Council on the date of the fall or winter meeting of the American Chemical Society I voted in favor of the September date in order that I might move a reconsideration of the question. I can not believe that the members of the Council, in voting as they have, gave due consideration to the following points which favor the December date:

1. A plan has been carefully formed to bring all of the scientific interests of the country together in one city once in five years. The December date was set in order to carry out this plan for the first time. It seems only fair that the chemists of the country should coöperate in carrying out this important scheme.

2. The date in September which is proposed is at a time when practically all of the professors and teachers in our colleges and universities are busy with the opening of the year's work and very few of this class of our members would find it possible to attend the meeting.

I move, therefore, that the motion fixing the date of the meeting in September be reconsidered.

I also move that in case the motion to reconsider carries the fixing of the date of the meeting be left to the Directors, or, if they prefer, postponed till the April meeting of the Council.

Very respectfully,

W. A. NOYES."

"February 29, 1916.

DR. CHARLES L. PARSONS, *Secretary*,  
American Chemical Society,  
Box 505, Washington, D. C.

*My Dear Dr. Parsons:*

In the recent letter ballot of the Council, held for the purpose of advising the President and Secretary as to the wishes of the Council regarding the time for holding the 1916 annual meeting, Dr. W. A. Noyes voted in favor of the September date in order to move a reconsideration. He now so moves, with the addition that in case of reconsideration the matter be left to the decision of the Directors.

Under the action of the Council at the 1911 Washington meeting it becomes my duty to pass upon the urgency of this motion.

While simultaneous action on the two motions is somewhat unparliamentary, nevertheless in view of the desirability of settling this matter as promptly as possible, I beg to certify to the urgency of Dr. Noyes' motion for reconsideration, and request that you will submit the matter to the Council immediately for letter ballot.

I regret that I cannot agree with the author of the motion in his desire that the annual meeting this year should be held in December, rather than in September as has been decided by the votes of so large a proportion of the Council.

Under normal conditions I would favor most heartily the policy of meeting quadrennially with the American Association for the Advancement of Science. At the Cincinnati meeting I spoke most earnestly in behalf of this policy, but this is an entirely different world from what it was at that time.

As a result of the European war chemistry has received a tremendous impulse in this country; the general public has been aroused to its importance to the welfare of the country; and this year of all others it is extremely desirable that we should have at our annual meeting the largest gathering of chemists that this country has ever known, for there are many problems, the solution of which demands personal conferences by men from every section of the country. There is need for the presence of both the men from the universities and the men of the industries at such conferences, and there is need of the greatest legitimate publicity of our work and aims.

I deeply regret that it was found absolutely impossible to hold the Second National Exposition of Chemical Industries during Convocation Week. Every effort was made to do so, but all of these efforts failed through inability to secure a suitable building during that week. The exposition must be held in September. If, therefore, we should decide to hold our annual meeting in December, I am confident that it would re-

sult in a large portion of our membership attending the Exposition and failing to attend the meeting of the Society. This would mean a very great loss in this particular year to the prestige and usefulness of the Society. The opportunity of a lifetime is in our hands. It seems to me that we would be very unwise to divide our strength just at the time when we have so wonderful an opportunity for increasing it.

Should the Council vote against reconsideration, members of the Society connected with universities would not be thereby necessarily prevented from attending the annual meeting. It seems reasonable that university authorities would gladly give leave-of-absence to members of chemistry staffs in those institutions which open on or before September 25th, and certainly the departments of chemistry in all of our universities would have much to gain from a meeting held in conjunction with the Second National Exposition of Chemical Industries.

Sincerely yours,

CHAS. H. HERTY, *President.*"

CHH :TAJ

Kindly signify your wishes by means of a cross, tear off ballot, and mail in inclosed envelopes to this office. Ballot is void unless it reaches me on or before March 23rd.

Yours very truly,

CHARLES L. PARSONS,  
*Secretary.*

1. ———In favor of reconsideration.

———Opposed to reconsideration.

2 If in favor of reconsideration.

———In favor of Dr. Noyes' request for immediate decision by the Directors.

———Opposed.

The above ballot was counted by a committee consisting of F. G. Cottrell, J. D. Davis, and Chas. L. Parsons. Ninety-seven ballots were cast, of which 31 were in favor of reconsideration, 61 opposed to reconsideration, and 5 illegal.

MEMBERS ELECTED BETWEEN FEBRUARY 15 AND MARCH 15, 1916.

Abbe, Paul O., 30 Broad St., New York City.

Alvord, Arthur L., 332 W. College Ave., State College, Pa.

Andrews, Joseph, 172 Church St., West Haven, Conn.

Bailey, Richard O., Oneida Community, Ltd., Oneida, N. Y.

Baker, Chas. F., Linden St., Meadville, Pa.

Ball, Albert E., 205 North Fourth St., McDonald, Pa.

Bateman, G. Alan, 503 N. Walnut St., West Chester, Pa.

Beckman, John Woods, 2215 Marin Ave., Berkeley, Calif.  
 Benjamin, Hugo S., Box 36, Big Stone Gap, Va.  
 Bentzen, F. W., 619 Ash St., Baraboo, Wisc.  
 Bernstrom, Harry O., 732 Comstock Ave., Syracuse, N. Y.  
 Bolte, C. Lawrence, 3757 Ellis Ave., Chicago, Ill.  
 Boyden, Sidney D., Battle Creek, Mich.  
 Brown, Henry C., c/o International Lead Ref. Co., East Chicago, Ind.  
 Buckley, Byron G., 112 W. Wood's Rd., Solvay, N. Y.  
 Bukacek, Adolph, North Dighton, Mass.  
 Bull, Hans, 4642 Penn St., Frankford, Philadelphia, Pa.  
 Burdett, Harold W., 25 Grove Ave., Leominster, Mass.  
 Bush, Burton T., 18 Platt St., New York City.  
 Camillus, Sister Mary, St. Xavier Academy, 4928 Cottage Grove Ave., Chicago, Ill.  
 Campbell, John Hayes, 2200 Insurance Exchange, Chicago, Ill.  
 Chambers, Alfred A., U. S. Geological Survey, Washington, D. C.  
 Clark, Paul W., 2235 Rose St., Berkeley, Calif.  
 Compton, J. N., 48 Y. M. C. A., Indianapolis, Ind.  
 Cooper, Hewitt W., Louisville Lead & Color Co., 223 N. 15th St., Louisville, Ky.  
 Crampton, Theo. H. M., Good Springs, Nevada.  
 Cronquist, G. Wson, Helsingborg, Sweden.  
 Dickson, J. V., 18 Callendar St., Toronto, Canada.  
 Doubleday, Arthur W., 220 Marlborough St., Boston, Mass.  
 Dure, Henry F., 103 McGraw Pl., Ithaca, N. Y.  
 Dyson, Robert E., 129 Bank St., St. Marys, Pa.  
 Edelstein, Oscar, 6 W. 116th St., New York City.  
 Elliott, Bruce S., 614 Bank of Commerce Bldg., St. Louis, Mo.  
 Elliott, Wesley A., Riverside Club, Pennsgrove, N. J.  
 Esten, Paul A., c/o Winslow Bros. & Smith Co., Norwood, Mass.  
 Fagan, J. Paul, 408 Sixteenth St., Ashland, Ky.  
 Fairbarin, G. K., No. Hoosick, N. Y.  
 Federer, Francis A., c/o Eli Lilly & Co., Indianapolis, Ind.  
 Findlater, Richard Hamilton, c/o Broxburn Oil Co., Ltd., Broxburn, Scotland.  
 Fleming, Alexander G., Canada Cement Co., Herald Bldg., Montreal, Canada.  
 Foley, Bart A., 90 Maiden Lane, New York City.  
 Foster, George H., 408 E. Springfield Ave., Champaign, Ill.  
 Gates, Ralph P., 21 E. 15th St., Chicago Heights, Ill.  
 Gillie, B. Austin, 186 Eighth St., Troy, N. Y.  
 Gillies, W. S., 6443 Kenwood Ave., Chicago, Ill.  
 Goldsmith, Henry Charles, 59 Hillside Ave., Newark, N. J.  
 Gononian, Y. H., 407 Classon Ave., Brooklyn, N. Y.  
 Guild, Carl, Royal Crown Soaps, Ltd., Winnipeg, Manitoba, Canada.  
 Hainsworth, W. R., 2657 Thirty-seventh Ave., S. W., Seattle, Wash.  
 Haley, D. E., University Club, State College, Pa.  
 Hauptli, Herbert A., 1012 S. Spaulding Ave., Chicago, Ill.  
 Hawse, Virgil P., Bureau of Mines, Pittsburgh, Pa.  
 Helfrich, John, 718 Land Title Bldg., Philadelphia, Pa.  
 Higgins, Emerson C., Jr., 54 East 33rd St., Bayonne, N. J.  
 Hill, W. K., 131 Wabash Ave., Carthage, Ill.

- Hiller, Harold M., 1554 Forty-ninth St., Brooklyn, N. Y.  
 Holmes, Edward Otis, Jr., 31 Greystone Rd., Malden, Mass.  
 Hood, Warren S., Baker House, Vineland, N. J.  
 Hughes, Wm. A., 25 Glenwood Blvd., Schenectady, N. Y.  
 Hundhausen, Herman C., Jr., Mercersburg, Pa.  
 Jacobs, Homer R., Delta Tau Delta House, Meadville, Pa.  
 Jenkins, S. M., 1 Liberty St., New York City.  
 Johnson, Maxwell O., U. S. Experiment Station, Honolulu, T. H.  
 Johnson, Oscar A., Malleable Iron Fittings Co., Branford, Conn.  
 Kammer, Glenn D., 5327 Beeler St., Pittsburgh, Pa.  
 Kimble, Evan E., Hotel Morlyn, Philadelphia, Pa.  
 King, H. H., Manhattan, Kans.  
 Kinsman, Arthur D., 80 County Rd., Ipswich, Mass.  
 Kocher, R. A., 1275 Seventh Ave., San Francisco, Calif.  
 Krase, Herbert J., 1103 Oregon St., Urbana, Ill.  
 Laird, Robert F., 606 Baer Bldg., Reading, Pa.  
 Lathwood, A., The Briars, Maidstone Rd., Bounds Green A., New Southgate, London, England.  
 Lehman, Walter Joseph, 573 Larchwood Ave., Philadelphia, Pa.  
 Lester, Joseph Henry, The Laboratory, Tootal Broadhurst Lee Co., Ltd., 56 Oxford St., Manchester, England.  
 Loeb, Clarence, Salisbury, Mo.  
 Macdonald, G. G., 87 Spadina Rd., Toronto, Canada.  
 Malinovszky, Andrew, Lincoln, Ill.  
 Marvin, Warren E., c/o Nestle's Food Co., Fulton, N. Y.  
 Matens, Campo E., Malvern, Pa.  
 Mickle, Friend Lee, State Water Survey, Urbana, Ill.  
 Middlekauff, J. Ellwood, Ensenada, Porto Rico.  
 Miller, Charlotte H., 307 Walnut St., Greensburg, Pa.  
 Mitchell, Singleton R., 200 N. Francisca Ave., Redondo Beach, Calif.  
 Mockaitis, John B., Villanova, Pa.  
 Morgan, Jerome J., 58 Pierson Rd., Maplewood, N. J.  
 Morton, Francis B., 41 Angell St., Providence, R. I.  
 Nelson, Wm. P., Jr., College Station, Texas.  
 North, C. E. H., 1554 Elizabeth St., Bremerton, Wash.  
 Norton, Charles L., Mass. Inst. Tech., Boston, Mass.  
 Noyes, Harry A., 335 W. Oak St., La Fayette, Ind.  
 Ornstein, Max Paul, 136 Attorney St., New York City.  
 Overstreet, John Boyd, College Station, Texas.  
 Pauline, Mother M., St. Mary's College & Academy, Norte Dame, Ind.  
 Payan, Eugene, St. Hyacinthe, P. Q., Canada.  
 Pfersch, C. L., 127 W. Lake Ave., Barberton, Ohio.  
 Pierce, Henry J., 913 Green Bldg., Seattle, Wash.  
 Pope, Frederick, 366 Fifth Ave., New York City.  
 Quam, G. Norman, 32 E. Dartmouth St., Vermillion, So. Dak.  
 Ramsdell, Leon E., 44 Riverview Rd., Brighton, Mass.  
 Rao, M. G. Srinivasa, 12 Sumner Rd., Cambridge, Mass.  
 Reed, Albert C., Latouche, Alaska.  
 Reid, Robt. R., Washington, Pa.  
 Schaum, C. W., 1213 No. 29th St., Philadelphia, Pa.  
 Selvig, W. S., U. S. Bureau of Mines, Pittsburgh, Pa.  
 Shields, Lewis W., Illinois Wesleyan Univ., Bloomington, Ill.

Sidnell, A. E., 340 N. Third St., Cuyahoga Falls, Ohio.  
 Simpson, A. Carson, Penna. Military College, Chester, Pa.  
 Smith, J. E., 60 $\frac{1}{2}$  Cottage St., Jersey City, N. J.  
 Spencer, A. Gordon, 4076 Tupper St., Westmount, Montreal, Canada.  
 Stehlby, E. T., 560 Washington Ave., Carnegie, Pa.  
 Sterne, L. M., 314 Williams St., Atlanta, Ga.  
 Stevens, Walter H., 1035 McFaddin Ave., Beaumont, Texas.  
 Stewart, W. H., 1720 L, C. Smith Bldg., Seattle, Wash.  
 Strang, Elmore S., Baltimore Tube Co., Baltimore, Md.  
 Strong, R. G., c/o Standard Sanitary Mfg. Co., Louisville, Ky.  
 Stuart, Elmer H., 704 Fletcher Ave., Indianapolis, Ind.  
 Sweet, Wm. L., 231 So. Main St., Providence, R. I.  
 Thomson, Procter, 3831 Jackson Blvd., Chicago, Ill.  
 Van Horst, Paul, P. O. Box 265, Tacoma, Wash.  
 Vaughn, Charles E., 45 Locust St., Springfield, Mass.  
 Waddell, K. M., Box 117, Albuquerque, N. Mex.  
 Wagner, Frederick D., 799 Putnam Ave., Brooklyn, N. Y.  
 Weisberg, Louis, 3210 Arthington St., Chicago, Ill.  
 Wheeler, George B., 1054 Dean St., Brooklyn, N. Y.  
 Wilson, J. C., c/o William F. Mosser Co., Richmond, W. Va.  
 Wilson, John L., 434 Somerville Ave., Olney, Philadelphia, Pa.  
 Wingate, W. Henry, 10 Highland Ave., Shelton, Conn.  
 Woo, Moi Lee, Spreckels, Calif.  
 Zacharias, W., Room 609 Hartje Office Bldg., Cor. Wood & First,  
 Pittsburgh, Pa.  
 Zentmire, Zelma, 210 Ash Ave., Station A., Ames, Iowa.  
 Ziser, George, 1210 Crown Hill Ave., Los Angeles, Calif.  
 Zolcinski, Ivan Petrovich, Mohsvaja 11, University, Moscow, Russia.

### MEETINGS OF THE SECTIONS.

[Full accounts of all meetings should be sent to Secretary Charles L. Parsons, Box 505, Washington, D. C.]

#### EASTERN NEW YORK SECTION.

The 64th meeting of the Section was held March 9th. The subject was, "The Electrolytic Refining of Copper," and the speaker, F. D. Easterbrooks, of Albany. Slides and pure chemical by-products were shown. The Society of Engineers of Eastern New York met with the Section.

ALBERT J. SALATHÉ, *Secretary*.

#### NEW YORK SECTION.

The fourth regular meeting was held in conjunction with the New York Section of the American Electrochemical Society and the Society of Chemical Industry, under the auspices of the American Electrochemical Society, February 11th.

The following papers were read: "Electrochemical War Supplies," by Lawrence Addicks (read by title); "Air Saltpeter," by W. S. Landis; "Hydrogen for Military Purposes," by E. D. Ardrey; "New War Products," by A. H. Hooker; "Magnesium," by W. M. Grosvenor; "Liquid Chlorine," by G. Ornstein; "Electrolytic Zinc," by W. R. Ingalls.



The fifth regular meeting was held March 10th. Program: Presentation of the William H. Nichols Medal to C. S. Hudson; "The Acetyl Derivatives of the Sugars," by C. S. Hudson; "Development of the Bureau of Chemistry," by Carl L. Alsberg.

The following officers were elected to serve the Section for 1916-1917, beginning July 1, 1916: J. M. Matthews, *Chairman*; F. J. Metzger, *Vice-Chairman*; C. F. Roth, *Secretary-Treasurer*; T. B. Wagner, Allen Rogers, C. M. Joyce, A. E. Hill, *Executive Committee*.

C. M. JOYCE, *Secretary*.

#### MILWAUKEE SECTION.

A meeting was held February 18th. Mr. F. W. Kressmann of the Forest Products Laboratory, Madison, Wis., gave an illustrated talk on, "The Uses of Wood Flour, Especially the Manufacture of Linoleum."

H. T. McALLISTER, *Secretary*.

#### CALIFORNIA SECTION.

The Section held its eighty-ninth regular meeting on February 15th in conjunction with the local Section of the American Institute of Mining Engineers.

The paper of the evening was given by Dr. Joel H. Hildebrand on, "The Fundamental Principles Underlying Flotation."

BRYANT S. DRAKE, *Secretary*.

#### EASTERN NEW YORK SECTION.

The 62nd meeting was held February 10th in conjunction with the Schenectady Section of the American Institute of Electrical Engineers and other scientific bodies. The address was given by Dr. John A. Brashear, Past President of the American Society of Mechanical Engineers, who took for his subject: "The Great Telescopes of the World and the Discoveries Made by Their Use."

The 63rd meeting was held jointly with the Theta Chapter of the Sigma Xi, February 11th. The speaker was Professor R. D. Kleeman, and the subject, "Ultra-Violet Light."

The 64th meeting was held March 9th. Program: "The Electrolytic Refining of Copper," by F. D. Easterbrook.

A. J. SALATHÉ, *Secretary*.

#### UNIVERSITY OF MISSOURI SECTION.

The 64th meeting of the Section was held February 18th. Dr. C. W. Greene addressed the Section on, "Some New Physiological Aspects of Fat Metabolism."

HENRY L. DAHM, *Secretary*.

#### KANSAS CITY SECTION.

The 112th meeting was held November 13th. Program: "The Fate of Food Protein in the Animal Body," by Dr. P. A. Shaffer.

The 113th meeting was held December 11th. Program: "High Alloy Steels for Long Span Bridges," by Dr. J. A. L. Waddell.

The 115th meeting was held February 19th. Program: "A Picric-Phosphotungstic Acid Clarifier for Sugar in Meat Extracts," by W. B. Smith; "Flotation," by George Belchic; "Heat Value of Gas of the Mid-Continental Field," by Prof. H. C. Allen.

W. B. SMITH, *Secretary*.

#### CHICAGO SECTION.

The regular meeting was held February 18th. Program: "The Present Status of Fertilizer Theory and Practice," by W. D. Richardson.

The regular meeting was held March 17th. Program: "The Chemistry and Metabolism of the Nucleic Acids," by H. Gideon Wells.

D. K. FRENCH, *Secretary*.

#### CINCINNATI SECTION.

The 203d regular meeting was held February 16th. Program: "The Application of Physical Chemistry to Some Geological Problems," by Otto Charles von Schlichten.

The 204th meeting was held March 8th. Program: "Various Aspects of the Smoke Problem," by Osborn Monnett.

ELLERY K. FILES, *Secretary*.

#### PUGET SOUND SECTION.

The Section held an open meeting in coöperation with the Manufacturers' Association February 26th. Program: "The Electrical Fixation of Nitrogen," by J. D. Roso; "Fisheries Products," by Geo. H. Stillson; "Potash from Kelp," by I. F. Laucks and H. Mahschmedt; "Potash from Mineral Resources," by G. A. Newhall; "Phosphate Rocks," by G. E. Weaver.

H. L. TRUMBULL, *Secretary*.

#### NASHVILLE SECTION.

The 38th meeting was held February 18th. Program: "The Utilization of Waste in the Manufacture of Copper," by Prof. J. T. McGill.

The 39th meeting was held March 17th. Program: "Estimation of Extract of Beef," by Prof. E. A. Ruddiman.

VICTOR P. LEE, *Secretary*.

#### NEBRASKA SECTION.

The February meeting was held February 19th. Program: "The Laboratory Examination of Clays," by Prof. George Borrowman.

H. M. PLUM, *Secretary*.

#### LOUISIANA SECTION.

The regular meeting was held February 18th. Program: "The Oxidation of Ethyl Alcohol by Means of Potassium Permanganate" (No. 2), by Jesse E. Day; "The Syrup Precipitate in the Direct Manufacture of White Cane Sugar," by C. E. Coates and L. C. Slater; "Some Notes on the Chemical Control of Petroleum Refineries," by C. E. Coates and M. M. Merritt.

F. W. LIEPMAN, *Secretary*.

#### ROCHESTER SECTION.

The regular meeting was held February 21st. Program: "Sewage Disposal," by C. C. Hopkins.

The regular meeting was held March 6th. Program: "The Photographic Microscope in Analysis," by Fred E. Wright.

H. H. TOZIER, *Secretary*.

#### AMES SECTION.

The fourth regular meeting was held March 2nd.

The Section was addressed by Dr. William D. Harkins, of the University of Chicago, on, "The Evolution of the Elements and the Periodic System."

W. G. GAESSLER, *Secretary*.

#### WASHINGTON SECTION.

The 258th meeting was held March 9th. Program: "The Action of Light on Chlorine with Special Reference to the Formation of Chloracetic Acid," by H. H. Curtis; "The Isolation of Vitamines from Brewers' Yeast," by A. Seidell; "On the Chemical Nature of Vitamines," by R. R. Williams.

E. C. McKELVY, *Secretary*.

#### ST. LOUIS SECTION.

The Section met March 6th. Program: "Activated Sludge," by Edward Bartow.

GEO. LANG, JR., *Secretary*.

#### CLEVELAND SECTION.

A special meeting was held February 23rd. Program: "Glass," by Alexander Silverman.

The March meeting was held March 13th. Program: "The Heat Temperature of Steel," by R. R. Abbott.

A. F. O. GERMANN, *Secretary*.

#### VIRGINIA SECTION.

The March meeting was held March 10th. Program: "The Revolution in Coke Manufacture and Its Relation to Our National Welfare," by Charles H. Herty.

W. A. BURROWS, *Secretary*.

#### UNIVERSITY OF MICHIGAN SECTION.

A meeting was held March 3rd. Program: "Glass Defects," by E. C. Sullivan.

H. H. WILLARD, *Secretary*.

#### CONNECTICUT VALLEY SECTION.

The 39th meeting was held March 11th. Program: "Electrical Precipitation of Flue Dust," by Mr. Egbert of the Research Corporation of New York City; "Manufacture and Testing of Cold Rolled Steel," by Mr. F. W. Shaefer, Stanley Works, New Britain.

R. J. MARSH, *Secretary*.

#### PHILADELPHIA SECTION.

The regular meeting of the Section was held February 24th. Program: "Modern Painting Practices on Structural Material," by George B. Heckel.

The regular meeting was held March 16th. Program: "The Chemistry of Glass Making," by Alexander Silverman.

J. HOWARD GRAHAM, *Secretary*.

## DETROIT SECTION.

The 79th meeting was held March 16th. "The Chemical Composition of Steel in Relation to Its Industrial Uses," by Jos. N. Bourg

EDW. J. GUTACHE, *Secretary*.

## WESTERN NEW YORK SECTION.

A meeting was held February 17th. Program: "Manufacture of Ice-cream," by Harry F. Lichtenberg.

The regular meeting was held March 3rd. Program: "The Chemistry of Photography," by F. C. Frary.

R. H. WHITE, *Secretary*.

## OREGON SECTION.

The 26th regular meeting was held February 26th. Program: "The Synthesis of Metals," by A. A. Knowlton.

NORMAN C. THORNE, *Secretary*.

## NEW HAVEN SECTION.

A meeting was held February 25th. Program: "On the Synthesis of Pyrimidine—Rosaniline Dyes," by T. B. Johnson; "On the Metallic Gallium and Some Gallium Reactions," by P. E. Browning; "The Effect of Freezing Precipitated Inorganic Colloids," by Blair Saxton; "An Apparatus for Determining Freezing-Point Lowering," by R. G. Van Name and F. G. Brown.

GEORGE S. JAMIESON, *Secretary*.

## MARYLAND SECTION.

The 12th regular meeting was held March 11th. Program: "By-Product Coke Oven Operation," by B. W. Winship.

FRANK M. BOYLES, *Secretary*.

## WISCONSIN SECTION.

The March meeting was held March 8th. Program: "The Electron Theory," by M. Mason.

L. F. AUGSPURGER, *Secretary*.

## LEXINGTON SECTION.

The 31st regular meeting was held March 9th. Program: "Investigations on the Abderhalden Test for Pregnancy," by W. S. Anderson; "The Duties of the United States Assay Commission," by F. E. Tuttle; "Some Queer Colloidal Precipitations," by C. A. Nash.

P. L. BLUMENTHAL, *Secretary*.

## MAINE SECTION.

A meeting of the Section was held March 3rd. Program: "Control of Sulfite Digestion by Titration Methods," by A. G. Durgin; "The Purchase Heat," by A. B. Andrews; "The Pulp and Paper Industry," by R. H. McKee.

E. O. WHITTIER, *Secretary*.

## DECEASED.

Martin Dennis, 859 Summer Ave., Newark, N. J., February 3, 1916.

# Proceedings.

## COUNCIL.

### Representatives of the American Chemical Society in the Organization for Industrial Preparedness.

ALABAMA.....	B. B. Ross.....	Auburn, Alabama
ALASKA.....	W. P. Lass.....	Speel River Electrochemical Co., Juneau, Alaska
ARIZONA.....	F. N. Guild.....	Tucson, Arizona
ARKANSAS.....	J. B. Rather.....	Agricultural Experiment Station, Fayetteville, Ark.
CALIFORNIA.....	Edmund O'Neill.....	Univ. of Calif., Berkeley
COLORADO.....	R. B. Moore.....	502 Foster Bldg., Denver
CONNECTICUT.....	E. W. Morley.....	West Hartford, Conn.
DELAWARE.....	Chas. L. Reese.....	Box 424, Chester, Pa.
DISTRICT OF COLUMBIA..	Chas. L. Parsons.....	Box 505, Washington, D. C.
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GEORGIA.....	F. N. Smalley.....	R. D. No. 2, Box 20, Savannah
IDAHO.....	J. S. Jones.....	Agric. Exp. Station, Moscow, Idaho
ILLINOIS.....	Wm. Hoskins.....	2009 W. Monroe St., Chicago
INDIANA.....	H. E. Barnard.....	State Laboratory of Hygiene, Indianapolis, Ind.
IOWA.....	W. F. Coover.....	Iowa State College, Ames, Iowa
KANSAS.....	W. A. Whitaker.....	University of Kansas, Lawrence, Kansas
KENTUCKY.....	A. M. Breckler.....	1801 1st St., Louisville
LOUISIANA.....	W. L. Howell.....	Room 315, Custom House, New Orleans, La.
MAINE.....	M. L. Griffin.....	Rumford, Maine
MARYLAND.....	W. B. D. Penniman...	6 E. Franklin St., Baltimore, Md.
MASSACHUSETTS.....	A. D. Little.....	93 Broad St., Boston
MICHIGAN.....	H. T. Graber.....	697 Trumbull Ave., Detroit

MINNESOTA.....	G. B. Frankforter.....	University of Minnesota, Minneapolis, Minn.
MISSISSIPPI.....	W. F. Hand.....	Agricultural College, Miss.
MISSOURI.....	L. F. Nickell.....	Washington University, St. Louis
MONTANA.....	E. P. Matthewson.....	Anaconda, Montana
NEBRASKA.....	C. F. Crowley.....	3315 Burt St., Omaha, Neb.
NEVADA.....	Maxwell Adams.....	Univ. of Nevada, Reno, Nev.
NEW HAMPSHIRE.....	H. K. Moore.....	P. O. Box 165, Berlin, N. H.
NEW JERSEY.....	H. S. Miner.....	Welsbach Light Co., Gloucester City, N. J.
NEW MEXICO.....	J. D. Clark.....	Univ. of New Mexico, Albuquerque, N. M.
NEW YORK.....	T. B. Wagner.....	Room 2229, 17 Battery Place, N. Y. City
NORTH CAROLINA.....	F. P. Venable.....	Chapel Hill, N. C.
NORTH DAKOTA.....	E. F. Ladd.....	Agric. College, Fargo, N. D.
OHIO.....	J. R. Withrow.....	Ohio State Univ., Co- lumbus, O.
OKLAHOMA.....	Edwin Debarr.....	Norman, Oklahoma
OREGON.....	O. F. Stafford.....	Eugene, Oregon
PENNSYLVANIA.....	R. F. Bacon.....	Univ. of Pittsburgh, Pittsburgh
RHODE ISLAND.....	J. E. Bucher.....	Brown Univ., Providence, R. I.
SOUTH CAROLINA.....	R. N. Brackett.....	Clemson College, S. C.
SOUTH DAKOTA.....	W. J. Sharwood.....	Lead, South Dakota
TENNESSEE.....	J. F. Norris.....	Vanderbilt University, Nashville, Tenn.
TEXAS.....	G. W. Gray.....	The Texas Co., Houston, Texas
UTAH.....	W. C. Ebaugh.....	208 Douglas St., Salt Lake City
VERMONT.....	G. W. Burrows.....	299 S. Union St., Bur- lington, Vt.
VIRGINIA.....	F. B. Carpenter.....	Virginia-Carolina Chem- ical Co., Richmond, Virginia

WASHINGTON.....	H. K. Benson.....	Univ. of Washington, Seattle
WEST VIRGINIA.....	A. R. Whitehill.....	Box 394, Morgantown, W. Va.
WISCONSIN.....	C. F. Burgess.....	625 Williamson St., Mad- ison, Wis.
WYOMING.....	R. B. Moudy.....	Laramie, Wyoming

MEMBERS ELECTED BETWEEN MARCH 15 AND APRIL 15, 1916.

Agostini, Carmelo, Jr., 397 Pulaski St., Brooklyn, N. Y.  
 Armitage, James F., c/o C. X. L., Beloeil Station, Quebec, Canada.  
 Babcock, S. C., 805 Ridge Road, Lackawanna, N. Y.  
 Beeman, Lyman, 625 Langdon St., Madison, Wisc.  
 Beers, Arthur D., 669 Maryland St., Gary, Ind.  
 Bennett, Clark H., 2209 Elston Ave., Chicago, Ill.  
 Boettner, Felix, Barrett Co., Frankford, Philadelphia, Pa.  
 Bonardi, J. P., Morgantown, W. Va.  
 Braun, Johannes, Box 294, Greenburg, Pa.  
 Bristol, Roland G., 254 Chapman St., Portland, Org.  
 Bruce, Edwin M., 1406 E. 57th St., Chicago, Ill.  
 Bunting, Herbert R., 2045 D St., Lincoln, Nebr.  
 Canfield, Joseph M., Jr., 607 Sixty-sixth Ave., Oak Lane, Philadel-  
 phia, Pa.  
 Cermelli, N. J., McMaster Club, Beloeil, Quebec, Canada.  
 Cummings, Tom, 6401 Steuart Ave., Chicago, Ill.  
 Curry, Gordon L., Louisville College of Pharmacy, Louisville, Ky.  
 Curtis, Francis J., 131 Otis St., Cambridge, Mass.  
 Dail, L. L., Ensley, Ala.  
 Dean, Reginald S., Rolla, Mo.  
 Deming, H. L., 702 Spruce St., Coffeyville, Kans.  
 Depree, F. J., 28 Van Alstyne Blvd., Wyandotte, Mich.  
 Dickhart, Wallace H., 243 S. 13th St., Philadelphia, Pa.  
 Draffin, Jasper O., 1009 W. Illinois St., Urbana, Ill.  
 Dreymann, C., Box 815, Baltimore, Md.  
 Duggar, J. F., Jr., 338 Main St., Pittsburgh, Pa.  
 Dunne, Peter, Morris & Co., Chicago, Ill.  
 Evans, Gwilym D., Atlas Powder Co., Landing, N. J.  
 Frizell, De Ralph, Shell Co. of California, Martinez, Calif.  
 Gilligan, F. C., Colonial Hotel, Copperhill, Tenn.  
 Gillinder, Edgar A., 1923 N. Park Ave., Philadelphia, Pa.  
 Gray, Harold, 1030 Leonard St., Indianapolis, Ind.  
 Gross, C. R., 361 Chem. Bldg., Urbana, Ill.  
 Grotts, Fred, Rolla, Mo.  
 Hamilton, E. D., Sumner High School, St. Louis, Mo.  
 Harter, R. W., Vermillion, S. Dak.  
 Herty, Chas. H., Jr., Chapel Hill, N. C.  
 Himmelein, Herbert T., 424 S. Weadock Ave., Saginaw, Mich.  
 Hoel, Archie B., 333 University Ave., Missoula, Mont.  
 Hollowell, Arthur J., 111 University St., W. Lafayette, Ind.  
 Huber, Donald W., 1421 Arch St., Philadelphia, Pa.

- Hughes, Walter S., 144 Randolph Ave., Milton, Mass.  
 Jenks, Philip D., 102 Chem. Bldg., Urbana, Ill.  
 Johnson, Carl L., Altoona, Kans.  
 Jones, Arthur, 3128 N. 25th St., Philadelphia, Pa.  
 Jordan, Claude W., 3101 Passyunk Ave., Philadelphia, Pa.  
 Julia, S., La Bedoule, B. du Rh., France.  
 Karr, Walter G., 407 W. Healey St., Champaign, Ill.  
 Kaufholz, Charles F., United Furnace Co., Canton, O.  
 Killefer, D. H., Chem. Lab., N. C. & St. L. Rwy. Shops, Nashville, Tenn.  
 Kindseth, Graham M., University of Arizona, Tucson, Ariz.  
 Kirkpatrick, Sidney D., 708 S. Goodwin Ave., Urbana, Ill.  
 Knapp, T. Edward, 1017 63rd St., Philadelphia, Pa.  
 Kuhns, Austin, 371 Harvard St., Cambridge, Mass.  
 Kullmann, Karl, 124 E. Davenport St., Iowa City, Iowa.  
 Lane, Walter J., 145 High St., Hartford, Conn.  
 Lavene, Harry A., 415 Jefferson Ave., Niagara Falls, N. Y.  
 Leaming, M. K., Morenci, Ariz.  
 Lehmann, Xavier M., 74 India St., Boston, Mass.  
 Leo, Shoo Tze, 705 S. Thayer St., Ann Arbor, Mich.  
 Levy, Gaston J., 619 Laurel Ave., San Mateo, Calif.  
 Linendoll, 50 E. Green St., Champaign, Ill.  
 Lumaghi, Octavius L., 4633 Berlin Ave., St. Louis, Mo.  
 McClugage, Harry B., 1003 W. Illinois St., Urbana, Ill.  
 McCormick, George T., 10802 Orville Ave., Cleveland, O.  
 McLeod, John G., Jr., 57 Fowler St., Dorchester, Mass.  
 McMullin, R. S., 116 Hyland Ave., Ames, Ia.  
 Meighan, Merl H., 723 E. Washington St., Iowa City, Ia.  
 Merrill, Allan B., 62 S. Balch St., Akron, O.  
 Minger, W. C., U. S. Mint, New Orleans, La.  
 O'Brien, John E., 3261 Martha St., Omaha, Nebr.  
 O'Neill, Frank V., 225 Bowdoin St., Dorchester, Mass.  
 Passmore, J. Faxon, 919 Gilpin Ave., Wilmington, Del.  
 Pelton, Earl L., 10 Grant St., Potsdam, N. Y.  
 Pierce, Edward W., Bala, Pa.  
 Pirrie, Noble W., Explosive Dept., Imperial Munitions Board, Ottawa, Canada.  
 Posin, Shalem E., 72 Graham Ave., Brooklyn, N. Y.  
 Railsback, John B., Forbing, La.  
 Rodgers, Clarence, Ky. Exp. Sta., Lexington, Ky.  
 Rollin, Hugh, Rolling Chemical Co., Charleston, W. Va.  
 Rowen, Robert, 13th & E. Wellens Ave., Philadelphia, Pa.  
 Rowland, Floyd E., 107 Chem. Bldg., Urbana, Ill.  
 Sands, Paul D., 264 S. 10th St., Philadelphia, Pa.  
 Schneider, 1825 S. Spring St., Springfield, Ill.  
 Schulze, John F. W., Turner Bros. Co., Terre Haute, Ind.  
 Schwamm, Chas. A., A. Chiris Co., Delawanna, N. J.  
 Sieck, W., Logansport, Ind.  
 Smith, Horace, Box 372, Humboldt, Tenn.  
 Smith, Robert F., 316 Huntington Ave., Boston, Mass.  
 Snyder, Andrew J., 114 Grand Ave., Waukesha, Wisc.  
 Spevakow, Nathan, 113 Thornton St., Revere, Mass.



Stack, Charles F., A. S. & R. Dem. Farm, Salt Lake City, Utah.  
 Steger, Alph., 58 Oldenbarneveltlaan, The Hague, Holland.  
 Steiber, Ward H., Mitchell, S. Dak.  
 Sutton, Charles W., Manchester Chemical Club, Manchester, Eng.  
 Tatsumi, Eiichi, Mitsui & Co., 25 Madison Ave., New York City.  
 Thorn, Wm. J., 1439 N. 62nd St., Philadelphia, Pa.  
 Titus, Charles P., 32 New St., East Orange, N. J.  
 Town, George G., 212 W. Gilman St., Madison, Wisc.  
 Treide, Henry E., 3408 Auchentoly Terrace, Baltimore, Md.  
 Treuting, Herbert R., 182 Willoughby Ave., Brooklyn, N. Y.  
 Trump, George S., Jersey Shore, Pa.  
 Valentine, John E. C., 1752 Barry Ave., Chicago, Ill.  
 van Senden, C. H., Shell Co. of Calif., Martinez, Calif.  
 Wakeman, Nellie A., 1814 Ray St., Madison, Wisc.  
 Walker, Frank E., 601 1st Nat'l Bank Bldg., Easton, Pa.  
 Warner, Philip B., 310 Lowell St., Peabody, Mass.  
 Weeks, Mildred W., 25th & E Sts., Washington, D. C.  
 Wenzel, Robert N., Box 826, Stanford University, Calif.  
 Werther, Sidney E., Box 112, Bisbee, Ariz.  
 White, Edward J., 9th & Westmoreland Sts., Philadelphia, Pa.  
 Witzel, H. W., 532 10th St., Niagara Falls, N. Y.  
 Zacharias, Procopios D., 22 Philhelinon St., Athens, Greece.  
 Zeller, Howard P., 2551 Fulton St., Toledo, O.  
 Zimmers, D. F., 310 Forbes Bldg., Pittsburgh, Pa.

#### CORPORATION MEMBERS.

Lindsay Light Co., 161 E. Grand Ave., Chicago, Ill.  
 Oliver Chemical Co., Mount Eden, Calif.  
 Westinghouse Lamp Co., Bloomfield, N. J.

### MEETINGS OF THE SECTIONS.

[Full accounts of all meetings should be sent to Secretary Charles L. Parsons, Box 505, Washington, D. C.]

#### CHICAGO SECTION.

The regular monthly meeting was held April 14th. Program: "Practical Vapor Pressures and Distillation," by Dr. M. A. Rosanoff, Mellon Institute, Pittsburgh, Pa.

D. K. FRENCH, *Secretary*.

#### LEXINGTON SECTION.

The 32nd regular meeting was held April 13th. Program: "Note on the Occurrence of Gallium," by Dr. R. N. Maxson. "A Recent Discovery with Reference to the Bang Bacillus," by Prof. E. S. Good. "The Separation and Estimation of Polysulfids and Thiosulfate in Lime-Sulfur Solution," by Mr. S. D. Averitt.

P. L. BLUMENTHAL, *Secretary*.

#### WASHINGTON SECTION.

The 259th meeting (special) was held March 21st. Program: Prof. John Uri Lloyd, of Cincinnati, "A Practical Demonstration of Some of the Principles of Colloidal Chemistry."

E. C. McKELVY, *Secretary*.

## MINNESOTA SECTION.

The Section met March 24th. Program: "The Factors Influencing the Occurrence of HCN in Plants," J. J. Willaman; "The Reimer-Tiemann Reaction," W. H. Hunter.

STERLING TEMPLE, *Secretary*.

## SOUTHERN CALIFORNIA SECTION.

The regular monthly meeting was held March 16th. The paper for the evening was presented by Mr. Wilhelm Hirschkind, Ph.D., on "The Bunsen Flame in Old and New Light."

H. L. PAYNE, *Secretary*.

## RHODE ISLAND SECTION.

The March meeting was held March 23rd. The speaker for the evening was Professor F. P. Gorham, of Brown University, who addressed the Section on "The Bacterial Treatment of Textile Fibers."

ROBERT F. CHAMBERS, *Secretary*.

## UNIVERSITY OF ILLINOIS SECTION.

The regular meeting was held March 21st. Program: "The Raw Materials of Varnish," Mr. C. T. Bragg, Chemical Engineer of the Ohio Brass Company.

G. D. BEAL, *Secretary*.

## LOUISIANA SECTION.

The 92nd meeting was held March 17th. Program: Dr. M. A. Schneller, "On the Determination of Diastatic Power in Wheat Flour." Mr. Wm. L. Owen, "The Influence of Phosphates on Alcoholic Fermentation." Mr. F. W. Liepsner, "Discussion of the By-products of Rice Milling."

F. W. LIEPSNER, *Secretary*.

## PUGET SOUND SECTION.

The March meeting was held March 25th. Program: C. E. Bogardus, "Opportunities for Electrochemical Industries." W. R. Hainsworth, "Bleaching Powder Costs." J. Daniels, "Artificial Abrasives." H. L. Trumbull, "The Production of Alkalies and Salts from Sea Water."

H. L. TRUMBULL, *Secretary*.

## SOUTH CAROLINA SECTION.

The 4th regular meeting was held December 10, 1915. Program: Dr. R. N. Brackett, "Abstract, Report of Referee Nitrogen Determination." Prof. C. F. Lipscomb, "Calomel Standard Cell, and the Various Thermodynamic and Thermochemical Relations Occurring in the Cell." Dr. J. E. Mills, "Gravitation." Mr. C. J. King, "A Note upon Methods for Determining Acidity in Soils." Mr. Boyden Nims, "The Relation of the State Laboratories to the Commercial Chemist." The election of officers was then taken up and the following were elected to hold office until the summer meeting of 1917: Dr. R. N. Brackett, *President*; Mr. C. T. Mayes, *Vice-President*; A. C. Summers, *Secretary-Treasurer*; Mr. Boyden Nims, *Councilor*.

A. C. SUMMERS, *Secretary*.

## UNIVERSITY OF MISSOURI SECTION.

The 65th meeting of the Section was held March 10th. Dr. Herman Schlundt gave a report on "The Methods of Radium Extraction from Carnotite Ore Used by the National Radium Institute at Denver, Colo."

A. G. LOOMIS, *Secretary*.

## OREGON SECTION.

The 27th regular meeting was held April 1st. Program: "Sulfur and Soil Acidity, Two Important Factors in the Fertility of Soils," Prof. H. V. Tartar.

NORMAN C. THORNE, *Secretary*.

## CONNECTICUT VALLEY SECTION.

The 40th regular meeting was held April 8th. Program: "Manufacture of Celluloid," Mr. Herbert E. Nims; "Some Analyses of Rocks from the Islands of the Pacific," Dr. E. W. Morley; "Browning of Gun Barrels," Mr. C. F. Wessell.

R. J. MARBE, *Secretary*.

## UNIVERSITY OF MICHIGAN SECTION.

The March meeting was held March 28th. Dr. F. E. Bartell presented a paper on "Negative Osmose."

H. H. WILLARD, *Secretary*.

## MARYLAND SECTION.

The 13th regular meeting was held April 15th. Program: "Coal Gas Residuals" (illustrated), by Dr. Frederick H. Wagner, of the Bartlett, Hayward Co.

FRANK M. BOYLES, *Secretary*.

## CLEVELAND SECTION.

The April meeting was held April 10th. Program: "The Microscope and its Accessories," Mr. L. B. Hall, of the Bausch & Lomb Optical Company, Rochester, N. Y.

A. F. O. GERMANN, *Secretary*.

## CINCINNATI SECTION.

The 205th regular meeting was held April 12th. Program: "The History, Characteristics and Methods of Manufacture of Modern Explosives," by Mr. M. F. Lindsley.

E. K. FILES, *Secretary*.

## IOWA SECTION.

A meeting was held April 8th. Program: "A Plant for the Manufacture of Synthetic Phenol," by Professor Harry McCormack, Head of the Department of Chemical Engineering, Armour Institute of Technology.

P. A. BOND, *Secretary*.

## VIRGINIA SECTION.

The April meeting was held April 14th. Program: "Some Chemical Classics," Dr. Garnett Ryland; "Some Phenomena of Lightning and Lightning Prevention," Dr. R. E. Loving; "The Relation of Research to Everyday Life," Dr. J. B. Weems.

W. A. BURROWS, *Secretary*.

## ROCHESTER SECTION.

The March meeting was held March 20th. Program: "The Character, Cost and Adulteration of Foods," by Prof. A. P. Sy, of the University of Buffalo.

A special meeting of the Section was held April 3rd. Program: "Velocity of Heterogenous Reactions with Especial Reference to Catalysis," by Dr. Irving Langmuir, from the Research Laboratories of the General Electric Co.

The regular meeting was held April 17th. Program: "The Organization of Industrial Research," by Dr. C. E. Kenneth Mees, Director of the Research Laboratories of the Eastman Kodak Company.

H. H. TOZIER, *Secretary*.

## SYRACUSE SECTION.

The 105th regular meeting was held March 24th. G. W. Cavanaugh, Professor of Agricultural Chemistry in Cornell University, spoke on "Some Problems in Agricultural Chemistry."

A special meeting was held April 7th. Mr. G. M. Berry, of the Halcomb Steel Co., spoke on "The Decennial of Electric Steel in America."

R. S. BOEHNER, *Secretary*.

## PITTSBURGH SECTION.

The 124th meeting was held February 17th. Program: "Thermal Reactions among Hydrocarbons at High Temperatures," by W. F. Rittman; "The Corrosion Resistance of Copper Steel," by D. M. Buck and J. O. Handy.

The 125th regular meeting was held March 16th. Program: F. C. Phillips, University of Pittsburgh, "Joseph Priestly;" Charles L. Parsons, Chief Chemist of the U. S. Bureau of Mines and Sec'y of the Amer. Chem. Society, "The Extraction of Radium from its Ores." W. C. COPE, *Secretary*.

## CALIFORNIA SECTION.

The 90th regular meeting was held March 25th. Program: "Some Problems in Paper Manufacture," by Mr. V. P. Edwardes; "A General System of Acids and Bases," by Dr. Merle Randall, Ph.D.

BRYANT S. DRAKE, *Secretary*.

## DECEASED.

Charles G. Carroll, University of Arkansas, Fayetteville, Ark., Feb. 22, 1916.

C. A. Catlin (Councilor A. C. S.), 133 Hope Street, Providence, R. I., April 12, 1916.

Gerald R. Donahoe, 510 Main St., Greensburg, Pa., Feb. 15, 1916.

Elton Fulmer, Agr. Exp. Station, Pullman, Washington, Feb. 20, 1916.

Harry C. Jones, Johns Hopkins University, Baltimore, Md., April, 1916.

Frank Kremer, Box 1608, Milwaukee, Wis., March 9, 1916.

G. E. Patrick, Dept. of Agriculture, Washington, D. C., March, 1916.

# Proceedings.

## GENERAL MEETING.

The 52nd meeting of the American Chemical Society was held at the University of Illinois, Urbana-Champaign, April 18th to 21st. A full account of the meeting will be found published on page 396 of the May issue of the *Journal of Industrial & Engineering Chemistry*. Five hundred and seventy-two members and one hundred and fifty-seven guests registered at the meeting, making it the largest meeting on record, no registration having been taken at the time of the New York meeting in conjunction with the 8th International Congress of Applied Chemistry. Members were present from thirty-two States, from Canada, Canal Zone, China and Japan.

The following Divisions met, titles of papers offered being already printed in the *Journal of Industrial & Engineering Chemistry* for May, page 462:

- Division of Agricultural and Food Chemistry.
- Division of Biological Chemistry.
- Division of Fertilizer Chemistry.
- Division of Industrial Chemists and Chemical Engineers.
- Division of Organic Chemistry.
- Division of Pharmaceutical Chemistry.
- Division of Physical and Inorganic Chemistry.
- Division of Water, Sewage and Sanitation.

The following business was transacted by the Divisions:

Division of Agricultural and Food Chemistry:

The meeting was called to order by Chairman L. M. Tolman on April 19th. Owing to the absence of the Secretary, the Chairman appointed M. B. Porch as acting Secretary. No business was transacted.

### DIVISION OF BIOLOGICAL CHEMISTRY.

In the absence of Chairman Alsberg, Vice-Chairman I. K. Phelps acted as Chairman of the Committee. There was extended discussion, especially on the papers bearing on colloid chemistry.

### DIVISION OF FERTILIZER CHEMISTRY.

The Division met with the regular officers present. No business was transacted. Reports of committees were discussed.

### DIVISION OF INDUSTRIAL CHEMISTS AND CHEMICAL ENGINEERS.

The Industrial Division met April 19, 20, 1916, with Dr. H. E. Howe presiding.

The Secretary reported a balance in the treasury of \$22.22.

It was voted that the Executive Committee be empowered to consider the revising of committees and to report at the New York meeting.

It was voted that the notice prescribed in Article VII of the By-Laws of the Division be sent to members before the New York meeting, as to a proposed amendment of Article IV.

It was voted that a Committee on Analysis of Fats and Oils, appointed by a number of manufacturers and buyers of fats and oils in the middle west and consisting of W. D. Richardson, Swift & Co., *Chairman*; P. Rudnick, Armour & Co.; A. Lowenstein, Morris & Co.; I. Katz, Sulzberger Sons & Co.; J. R. Powell, Armour Soap Works; H. J. Morrison, Proctor and Gamble; Ernst Twitchell, Emery Candle Co., be taken over by the Division and be known as the Committee on the Analysis of Fats and Oils.

It was voted that the Chairman appoint a committee to be known as the Committee on Analysis and Specifications of Cotton Seed Products.

It was voted that the members of the Division be assessed one dollar each for the purpose of defraying Divisional expenses.

#### Executive Committee Meeting:

The Executive Committee of the Division met on the afternoon of April 20th, the following members being present: H. E. Howe, *Chairman*; S. W. Parr, C. H. Herty, J. R. Withrow, S. H. Salisbury, Jr.

The Committee indorsed the Division's action with regard to the amendment of Article IV of the By-Laws so that certain committees need not be appointed.

The Committee indorsed the action of the Division with regard to the taking over of the Committee on the Analysis of Fats and Oils.

The Committee favored the appointment of a Committee on the Analysis and Specifications of Cotton Seed Products; but agreed that any methods made necessary by sudden changes of conditions in the Industry should not have the authorization of the Society until they had passed through the regular channels.

It was voted that the program for the New York meeting consist largely of conferences rather than so many regular papers.

It was voted that an advisory committee be appointed to determine the length of time a paper shall have on the program.

The Committee favored the suggestion that papers, of which an abstract is submitted to the committee before the meeting, be allowed five minutes and that the committee shall allow more time at their discretion.

The Committee favored the suggestion that the author of a paper give, before the Division, the object of his work and a summary of the results and leave the details to be brought out in discussion.

S. H. SALISBURY, JR., *Secretary*.

#### DIVISION OF ORGANIC CHEMISTRY.

The Division met with the regular officers present. No business was transacted.

### DIVISION OF PHARMACEUTICAL CHEMISTRY.

The Division met with the regular officers present. No business was transacted.

### DIVISION OF PHYSICAL AND INORGANIC CHEMISTRY.

The following motion was unanimously passed:

"That a committee of three be appointed by the chair to arrange the program of the Division of Physical and Inorganic Chemistry for the September meeting of the Society. No paper exceeding five minutes in length shall be read before the Division unless an abstract is received by the Committee and approved by them. No member shall present more than one paper before the Division unless an abstract of each paper be received and approved by the Committee."

The Division appointed James Kendall, W. D. Bancroft, and Colin G. Fink as the program committee for the annual meeting.

The Chairman of the Division, Irving Langmuir, was present and presided.

### DIVISION OF WATER, SEWAGE, AND SANITATION.

The Division met with Chairman Edward Bartow in the Chair. R. B. Dole was elected Secretary, *pro tem*.

The following report of the Committee on Standard Methods for the Examination of Water and Sewage was presented and accepted:

The chief methods which have been added to the Second Edition of Standard Methods of Water Analysis published by the American Public Health Association and now being revised by your committee in collaboration with a committee of the American Public Health Association and the Referees of the Association of Official Agricultural Chemists are methods for the examination of sewage sludge and muds, for chemicals used in water treatment, and for available chlorine. The diction of the former edition has been extensively revised in the interest of attaining unity and clearness. The methods have been rearranged in groups and classified in order to make them more logical. The determinations of total acidity by titration with sodium carbonate in the presence of phenolphthalein, of manganese by Knorre's volumetric persulfate method and by the lead peroxide method, of lime and soda value and of caustic alkalinity by the silver nitrate method will be omitted from the third edition. This edition is now in galley proof.

As above indicated, details of the meeting and of the papers offered to the various Divisions will be found in the May issue of the *Journal of Industrial & Engineering Chemistry* and need not be reprinted here.

CHARLES L. PARSONS, *Secretary*.

## DIRECTORS' MEETING.

The Directors of the American Chemical Society met in the Chemistry Building of the University of Illinois on Wednesday morning, April 19, at 11 o'clock, with President Herty in the chair and Directors Bigelow, Bogert, Parsons, Smith and Whitney present.

The payment of \$1,800 by the Finance Committee to The Chemists' Club on account of the Morris Loeb Museum fund was approved by the Directors.

The recommendation of the Council regarding the printing of the ten-year index to *Chemical Abstracts* was considered by the Directors and formally approved by them. It was voted that Mr. Crane be authorized to proceed with the compilation of this index, employing the necessary assistance therefor on the basis of his estimate of \$6,500 for compilation purposes; that he be authorized to obtain bids for the printing of the index and to present these to the Directors for further action at their December meeting.

It was voted that the price for the index to *Chemical Abstracts*, unbound, be \$10.00 to members subscribing up to January, 1917; thereafter the price should be \$12.00 to members. It was voted that the price to all non-members of the Society subscribing after the announcement to be made in the May 10 issue of *Chemical Abstracts* should be \$15.00.

It was voted that the Secretary be authorized to solicit and receive subscriptions from chemical manufacturers toward the cost of publishing the ten-year index to *Chemical Abstracts*, as it was estimated that the cost of publishing would be about \$10,000 in excess of the \$20,000 advance subscriptions already received.

It was voted that such part of \$75.00 as may be necessary to meet the expenses of the Allyn Committee be appropriated.

It was voted to appropriate the usual annual contribution of \$100.00 to the Annual Tables of Physical & Chemical Constants, and an extra \$100.00 owing to the special difficulties which our foreign colleagues have to meet at the present time.

The question of advertising rates in the journals of the American Chemical Society was discussed by the Directors. It was voted to ask Messrs. E. G. Love, M. C. Whitaker, and B. C. Hesse to act as an Advertising Committee for the Directors during the year 1916. The Secretary was directed to request the Advertising Committee to consider at once the question of an advance in the rates of advertising in our journals and take early action thereon, as the Directors considered the matter urgent.

CHARLES L. PARSONS, *Secretary*.



## COUNCIL.

President Herty appointed the following to represent the Society on the occasions noted after their names:

M. T. Bogert, Chas. L. Parsons, George D. Rosengarten, Edward Bartow, H. E. Barnard—Spring Meeting of the National Conservation Congress.

T. W. Richards—Dedication of the New Buildings of the Massachusetts Institute of Technology.

Leroy W. McCay—Celebration of the 150th Anniversary of the Founding of Rutgers College.

### Minutes of the Council Meeting.

The Council of the American Chemical Society met in the Chemical Building of the University of Illinois on Monday, April 17, at 8 P.M., the following councilors being present: Atkinson, F. C.; Bailey, E. H. S.; Bancroft, W. D.; Barton, G. E.; Bartow, Edward; Bigelow, W. D.; Bogert, M. T.; Boyles, F. M.; Bryan, T. J.; Byers, H. G. (substitute); Campbell, A.; Chamot, E. M.; Coover, W. F.; Crane, E. J.; Derick, C. G.; Fischer, Richard; Frankforter, G. B.; French, D. K.; Goldbaum, J. S.; Henderson, W. E.; Hendrixson, W. S.; Hollinshead, W. H.; Howe, H. E.; Hudson, C. S.; Hunter, W. H.; Johnson, T. B.; Johnston, John; Jones, Grinnell; Jones, L. W.; Langmuir, Irving; Lowenstein, Arthur; Mabery, C. F. (substitute); Magruder, E. W.; Nickell, L. F. (substitute); Noyes, W. A.; Parr, S. W.; Phelps, I. K.; Phillips, F. C.; Schlundt, Herman; Smith, Alexander; Sosman, R. B.; Stieglitz, Julius; Talbot, H. P.; Taylor, A. N. (substitute); Tolman, L. M.; Tower, O. F.; Tuttle, F. E.; Washburn, E. W.; Watkins, W. H.; Whitney, W. R.

The appointment of Mr. W. B. Price as representative of the American Chemical Society on the Committee of the Institute of Metals Advisory to the Bureau of Standards was approved.

The appointment of Dr. Charles Baskerville to represent the American Chemical Society on the "Joseph A. Holmes Memorial" Committee was approved.

The death of Mr. Charles A. Catlin, Councilor since 1898, was announced to the Council. A committee consisting of W. R. Whitney, W. A. Noyes, and H. P. Talbot was appointed to draw up suitable resolutions to be transmitted to the family of Mr. Catlin and to be published in the *Journal of Industrial & Engineering Chemistry*.

It was voted to establish a local section with headquarters at Burlington, Vt., with territory covering the State of Vermont, as soon as a waiver of jurisdiction can be obtained from the Northeastern Section.

It was voted to continue the towns of Sewanee and Richard City, Tenn., in the territory of the Nashville Section.

It was voted to establish a local Section with headquarters at Vermilion, S. D., including the territory of the State of South Dakota.

It was voted to refer to the editors, with power, the question of reversing the order of publication of the *Journal of Industrial & Engineering Chemistry* and the *Journal of the American Chemical Society*.

The invitations from the Kansas City Section of the American Chemical Society and from the University of Kansas to hold the Spring meeting of 1917 in Kansas City, Mo., and in Lawrence, Kansas, were accepted.

A communication was presented to the Council by E. J. Crane, Editor of *Chemical Abstracts*, showing that nearly Twenty Thousand Dollars has been raised by subscription from members of the American Chemical Society for the printing of a ten-year index to *Chemical Abstracts*, and that Thirty Thousand Dollars would be required to print the necessary number of copies. After discussion, it was moved that the Council recommend to the Directors that a ten-year index to *Abstracts* be published in 1917.

A letter from Mr. Thomas B. Freas, of Columbia University, New York City, was presented to the Council by Professor Alexander Smith, regarding the question of duty-free importations of chemical apparatus. It was voted to appoint a committee to consider the whole matter and report at the next meeting of the Council. President Herty appointed a committee consisting of Alexander Smith, Chairman, Arthur H. Thomas, and Wm. McPherson.

Upon request of the Bureau of Mines, a committee of the American Chemical Society, of whom President Herty should be chairman, was appointed as an advisory committee to the Bureau of Mines on chemical problems in connection with its investigations. The committee consists of C. H. Herty, L. H. Baekeland and W. R. Whitney.

The Council passed a unanimous vote of thanks to the following organizations and individuals for efficient assistance given by them toward the success of the Urbana meeting:

President Edmund J. James and the Trustees of the University of Illinois, for their interest and coöperation.

Chamber of Commerce, Champaign, Illinois, C. W. Murphy, Managing Secretary, for their part in the complimentary smoker.

Commercial Club, Urbana, Illinois, W. D. Miles, Secretary, for their part in the complimentary smoker.

Professor Isabel Bevier, Woman's Building, University of Illinois, Chairman of the Ladies Committees, and the members of the Committee, for the entertainment of the ladies.

Dr. H. L. Olin, Chemistry Building, University of Illinois, and Mr. A. N. Bennett, of State Water Survey, Urbana, Illinois, for organizing and superintending the exhibit of chemical industries.

Professor J. M. White, Supervising Architect, Administration Building, University of Illinois, for coöperation with the committee in making plans for the meeting and in the efficient services given by himself and his assistants before and during the meeting.

John Glover, Illinois Traction Company, Urbana, Illinois, for coöperation in planning and carrying out the special excursion to Danville.

H. J. Pepper, Superintendent Street Railway Co., Champaign, Illinois, for arrangements for special cars after the council meeting, smoker and banquet.

Danville Chamber of Commerce, Danville, Illinois, P. L. Wills, Secretary, for entertainment of the Society at luncheon.

J. W. Hegeler, President Hegeler Zinc Co., Danville, Illinois, for privilege of visiting the Hegeler plant.

W. G. Hartshorn, President, Two Rivers Coal Co., Danville, Illinois, for arrangements for visit to the strip coal mine and the special trouble he took to have the plant operated for the members of the Society.

F. W. Butterworth, Danville, Illinois, General Manager, Western Brick Company, for permission to visit the plant of the Western Brick Company.

Danville Rotary Club, Thomas J. Corsey, Secretary, Danville, Illinois, for their assistance in entertaining the members of the Society.

Illinois Window Glass Co., Chas. Robasse, Manager, Danville, Illinois, for the privilege of visiting the works of the glass company.

Major R. W. Mearns, 12th Infantry, U. S. A. Commandant, University of Illinois, for the arrangements for the brigade drill.

Professor A. A. Harding, Director of the University of Illinois Band, for the band concert.

McIntosh Stereopticon Co., 30 E. Randolph St., Chicago, Illinois, for furnishing lanterns for all of the sectional meetings and for the courtesy and efficiency of Mr. Price, the manager.

Dean E. Davenport, Agricultural College, University of Illinois, for arrangements for visits to the Agricultural College and especially for the assistance rendered by Professor Rankin and Mr. Checkley in planning the excursion and in carrying it out.

Dean W. F. M. Goss, College of Engineering, University of Illinois, for visit to the Engineering College, especially to B. W. Benedict in arranging the program and carrying it out.

G. D. Worthington, Hotel Beardsley, Champaign, Illinois, for his successful management of the banquet and for his interest and coöperation in caring for the members of the Society.

F. R. Smedley, District Deputy, Grand Master, Order of Masons, Champaign, Illinois, for his kindness in allowing us the use of the banquet room and first floor of the Masonic Temple for an assembly room and for cloak room.

Cosmopolitan Club, Champaign, Illinois, for their part of the entertainment at the smoker.

Mr. H. A. Winkelmann, Chemistry Building, University of Illinois, for his management of the checking arrangements at the banquet and Mr. W. F. Langelier for his management of the checking arrangements at the smoker.

Chairmen and members of the local committees to whom the success of the meeting was chiefly due.

It was voted that the reports of the Committee on Water Analysis and the Committee on Coal Analysis be adopted and approved by the American Chemical Society when these reports have received the approval of the Supervisory Committee on Standard Methods of Analysis.

The committee of the American Chemical Society consisting of Julius Stieglitz, Lauder W. Jones, Lucius P. Brown, A. D. Thorburn, and E. H. S. Bailey, presented the following report, which, after discussion and minor amendment, was unanimously adopted in the following form by the Council:

#### **Report of the Committee on the Westfield Campaign and Mr. Lewis B. Allyn's Connection Therewith.**

Your committee begs to report as follows:

I. After due consideration of the facts and evidence presented we recommend that no further action be taken leading to the expulsion of Mr. Lewis B. Allyn from our Society, and we recommend that the St. Louis Section be so informed.

II. Special pure food movements, of which the so-called Westfield campaign is but one, seem to have originated and received their impetus from the recognition of the fact that the public desires a positive guarantee of the purity of foods and of toilet preparations. This demand is indeed appreciated by public officials but the recognition in a positive sense, of individual articles is as yet the exception and not the rule. The most common form of public service in this field by the national government, the states, the municipalities, consists rather in exposing misbranded or fraudulent preparations, in prosecuting infringements of the law and in assisting manufacturers to comply with legal requirements.

On the other hand, those special movements which have been exploited by magazines and other publications in connection with their advertising columns must be considered *altogether wrong in principle and opposed to the best interests of the public*. The following are the reasons leading to this conclusion. All or part of them apply, we believe, to the various individual forms, which movements of this kind have taken.

(1) Almost without exception, profiting financially by means of advertising is directly connected in one way or another with such campaigns. The movements are therefore not *disinterested*. In the very nature of the case pressure is quite likely to be exerted by advertising departments on the editorial department and on the policy of the publication. A bias may thus be created, which has no proper place in matters demanding purely scientific and judicial decisions. This bias in debatable cases, will often lead men, consciously or unconsciously, to yield to private gain rather than to public interests. Furthermore, for the sake of large financial returns, such a campaign is almost certain to be used by some agent or other, such as the advertising manager, to bring what must be considered an illegitimate kind of pressure to bear on those who advertise food products or toilet preparations, to have their advertisements appear in the publication conducting the campaign. Such a campaign in itself must be considered a form of unfair coercion.

(2) Special campaigns of this character have neither the large means nor the high scientific standing needed to secure a really efficient and reliable guarantee to the public. Any guarantee which they afford may become utterly worthless, and, by inducing a false sense of security, may indeed do positive harm, if it is not supported by *continuous* control, including unexpected examinations, and by persistent official inspection covering all phases of food control, such as the inspection of the places and methods of manufacture, their sanitary surroundings, and the quality and condition of materials used. The public control of the milk supply, as it has developed in recent years in some of our larger municipalities, is an illustration of what adequate control must aim at.

In the light of all experience these special campaigns are likely to be supported by wholly inadequate chemical and bacteriological staffs and by altogether insufficient forces of inspectors, for the indispensable routine work of the thorough-going and continuous control by analysis and inspection. This defect, quite aside from motives of gain underlying a campaign, makes such a propaganda a very questionable value to the public.

(3) In place of developing and adopting standards on the basis of exhaustive and authoritative investigations by men of the highest scientific training and experience and of obviously disinterested motives,

such campaigns as a rule depend on the dictum of some single self-constituted "authority," possibly having little or no scientific standing, often of narrow training and experience. Proper organization of such a movement demands facilities for disinterested scientific investigations by a staff of chemists, bacteriologists, physiologists and physiological chemists, or at least should depend for its final authoritative control on the combined judgment of a group of men of special training and recognized standing in these lines of scientific work.

III. In view of the defects of endorsement of preparations by special food movements, as exploited by magazines and other publications, and in order that the just demand of the public for positive information guaranteeing the purity of food and toilet articles, may be properly satisfied, the committee would urge that the Society consider formulating plans to be laid before governing bodies, which would lead to some kind of direct certification of food and toilet articles, by the national government, by properly organized and equipped departments of the states and larger municipalities, or some other forms of responsible control.

The preparation of a detailed plan involves questions of considerable difficulty, which the short time at the disposal of the committee has not made it possible for its members to study and decide. The committee, therefore, recommends that the formulation of such plans be referred to a special committee of the Council.

(The following paragraph of the report of your committee was proposed and endorsed by the non-official members of the committee:)

These larger plans for public control are so much more justified as the Council of the American Chemical Society, in common with all well informed men, knows that the country has reason to have the highest degree of pride and confidence in the integrity, the disinterestedness and the competent character of the work done in the past and at present by the men engaged in the government food control.

An expression of thanks was unanimously voted to Dr. Stieglitz and the members of his Committee for their efficient handling of this difficult problem.

The following two suggestions of amendments to the By-Laws were presented by the Committee appointed to consider the Allyn matter:

1. The Chairman of the Committee on Membership shall submit a monthly report for publication in the Proceedings of the Society which gives the name, residence, and occupation of each nominee, and the names and residence of his nominators. Final action shall be taken by the Committee on these names only after thirty days have elapsed since the publication in the Proceedings.

2. Any motion for the expulsion of any member of the Society shall

be submitted first in confidence (without further divulging the name of the member) to the President of the Society with a full statement of the *prima facie* evidence on which the motion is based. The President, in conjunction with the two ex-Presidents preceding him most immediately in office, shall form a committee with full power to decide whether the motion shall be dropped without further action and without report to the Council; whether the accused member shall be allowed to resign without report to the Council, or whether the motion shall be referred, without prejudice, to a special committee of the Council for further investigation and report to the Council.

After some discussion the Council voted to refer these two amendments to a committee of three to be appointed by the President to prepare a report and submit same to the Secretary in time to present to the Council for action at the September meeting. The President appointed W. A. Noyes, M. T. Bogert, and F. K. Cameron.

On the motion of Mr. H. E. Howe it was voted that a committee be appointed to consider the formation of a publicity bureau, whose duties shall include the publication of chemical articles to offset objectionable matter so often appearing in the public press. The President appointed H. E. Howe, Ellwood Hendrick, and A. V. H. Mory.

The following committees reported to the Council:

Committee on Patent Legislation:

Report will be printed in full in the *Journal of Industrial and Engineering Chemistry*.

Committee on Inventions by Government Employees presented to the Council a statement of present conditions, but made no recommendations. The report was placed on file.

A statement was received from the Chairman of the Committee on Professional Ethics, but as the matter had not received the approval of the full Committee, it was voted to continue the Committee and request them to complete their report and submit same to the Council in writing in advance of the meeting at which it is to be considered.

The Supervisory Committee on Methods of Analysis reported as follows:

In accordance with the provision of the Constitution, relative to Standing Committees, I submit to you, for presentation to the Council, my report as Chairman of the Supervisory Committee on Methods of Analysis, covering the period since March 17, 1915, the date of my last report (Proceedings, 1915, p. 50).

#### I. COMMITTEES OF THE GENERAL SOCIETY.

##### 1. *Committee on Revision of Methods of Coal Sampling and Analysis.*—

A joint committee representing the American Chemical Society and the American Society for Testing Materials.

A final report of the above named committee was submitted to the American Society for Testing Materials at its meeting last Summer. According to the rules of that Society, such a report must be considered tentative for one year. The report has received the unanimous approval of the committee of our own Society and upon final adoption by the coöperating Society will be submitted to the Supervisory Committee on Methods of Analysis for acceptance on behalf of the American Chemical Society.

There are some important considerations connected with coal analysis still under discussion among the chemists of the country, especially the question of the fusibility of the ash of coal and methods for the analysis of coke, which are now in the hands of another committee with which the Committee on Coal Analysis is coöperating. On this account both societies will be asked to continue the joint committee.

2. *Committee on Methods of Analysis of Potable Waters and Sewage.*—A committee of the American Chemical Society, working in conjunction with one from the American Public Health Association and with representatives of the Association of Official Agricultural Chemists.

The report has been completed, but will be submitted for final criticism before adoption by the Water, Sewage, and Sanitation Division of the American Chemical Society and the Laboratory Section of the American Public Health Association.

## II. DIVISIONAL COMMITTEES.

A. Division of Industrial Chemistry and Chemical Engineers. Chaos still rules with respect to the relation to each other of the Committees of this Division.

1. *Committee on Standard Specifications and Methods of Analysis.*—This committee still lacks a head and has been entirely inactive during the year. Committees supposedly under its control, if active, are acting independently of it.

(a) *Committee on Non-Ferrous Metals and Alloys.*—The reports on copper and spelter from this committee referred to in my report of last year, having received the approval of the Supervisory Committee on Methods of Analysis, were printed in the *Journal of Industrial and Engineering Chemistry*, 7, 546-7. The committee has had to postpone further work for the present.

(b) *Committee on Soap and Soap Products.*—No active work has been done by this committee, but a tentative set of methods will be considered at the Urbana meeting of the Society for trial by the committee and those who may be willing to coöperate. It is proposed that where the methods overlap the work of other committees in and outside of the



Society, they be coördinated. For the better attainment of this result it is suggested that two outside committees be recognized as committees of the Division.

(c) *Committee on Glycerine*.—At present this is a sub-committee of that on Soap and Soap Products, but the latter committee is disposed to recommend to the Division that it be given independent standing. The Chairman of the Glycerine Committee has in preparation an article on the bi-chromate method for the determination of glycerine and a new specific gravity table based on a new method of preparing pure glycerine.

#### B. Division of Fertilizer Chemists.

1. *Committee on Research and Methods of Analysis*.—Nothing has been learned regarding the work of this committee and of its several sub-committees, notwithstanding the efforts made by myself to secure reports.

#### C. Division of Pharmaceutical Chemistry.

1. *Committee on Quantitative Methods*.—No work done during the year.

#### D. Section of Rubber Chemists.

1. *Committee on Analysis of Rubber and Rubber Products*.—This committee has been inactive during the year. The Chairman writes that the committee needs reorganizing in consequence of the resignation of two of its members and the inability of a third to do active work.

W. F. HILLEBRAND, *Chairman*.

The Committee on Occupational Diseases presented the following report:

1. The Committee on Occupational Diseases in Chemical Industry purposes having a symposium on the subject at the New York Meeting of the Society.

2. The unusual development of coal-tar color and explosives industries in the United States, due to the War, has laid some emphasis upon the necessity for improving ventilation and taking more care to destroy certain fumes as precautions against occupational diseases arising from their inhalation. Information as to several such cases has come to hand.

3. A surgeon of the United States Public Health Service has been specially assigned to the study of Occupational Diseases. He is at present carrying on his investigations in the Pittsburgh district.

4. The effort at the enactment of a *uniform* law in all the states in regard to wood alcohol has progressed by its introduction in the Legislatures of Kentucky and New York.

5. Trouble arising from dust of vanadium ores has been overcome at the Denver radium plant by suitable dust removers. The use of sponges over the noses and mouths of the men sampling iron vanadate at the same plant has not proved to be a sufficient protection. After a few

hours' work the men cough and get a feeling of lassitude with a tightness in the chest and throat. If the work be continued, pains follow. The effects wear off after a few days' rest. No permanent injury has been reported.

6. An investigation of the pathological effects of Port Oxford Cedar dust is under way.

Respectfully submitted,

CHAS. BASKERVILLE, *Chairman.*

The Committee on Exchanges reported that fourteen new exchanges had been put into effect during the past year; that three old exchanges had been discontinued, and five offers to exchange had been declined.

The Finance Committee reported as follows:

The Finance Committee begs to report for the fiscal year ending November 30, 1915, that the financial affairs of the Society are in a very satisfactory condition.

The Report and Balance Sheet submitted by the Treasurer have been properly audited by certified Public Accountants, under the direction of the Committee, and the same have already been printed in the Proceedings for February.

During the year New York City Bonds to the amount of \$2,000, at  $3\frac{1}{2}\%$ , which fell due in October, were re-invested in similar bonds at  $4\frac{1}{2}\%$ .

Since the close of the last fiscal year, the Society, as Trustee of the Morris Loeb Museum Fund, has paid to The Chemists' Club \$1,800, making a total of \$2,500 paid to the Club under the Trust.

Respectfully submitted,

E. G. LOVE,

G. C. STONE,

A. E. HILL,

*Finance Committee.*

The Committee on Paper reported that they had carefully followed the quality of the paper used in the Society's publications during the past year; that the quality had not been entirely up to specifications, but that they hoped this could be remedied in the future.

The Committee on Membership reported that during the past year 877 members have been elected, two Corporation Members and one Honorary Member.

The Perkin Medal Committee reported the awarding of the Perkin Medal for 1916 to Dr. Leo H. Baekeland, of Yonkers, N. Y.

The American Chemical Society representative on the Committee on Supervision of the Chemical Engineering Catalog reported progress, and

that the assistance of the Committee had been of value to the publishers. It was reported that they hoped such a Chemical Engineering Catalog would be issued during the coming Fall.

Professor F. C. Phillips presented a communication to the Council regarding a memorial to Joseph Priestley. Professor Phillips' report had been previously presented to the Pittsburgh Section of the American Chemical Society; had been adopted by them and recommended to the Council of the Society. The Council voted that the President should appoint a committee to decide upon a Priestley Memorial, with power to carry out their conclusions and to solicit funds therefor. President Herty appointed the following committee: F. C. Phillips, *Chairman*; M. T. Bogert, E. D. Campbell, F. W. Clarke, E. C. Franklin, J. Lewis Howe, J. H. Long, E. W. Morley, A. A. Noyes, W. A. Noyes, Ira Remsen, Alfred Springer, F. P. Venable, C. F. Chandler.

The following committees have been appointed for 1916-17 by President Herty:

Committee for Annual Report on Atomic Weights: G. P. Baxter.

Committee on Exchanges: E. J. Crane, *Chairman*; W. A. Noyes, M. C. Whitaker.

Finance Committee: E. G. Love, *Chairman*; A. E. Hill, G. C. Stone.

Committee on Methods of Analysis for Potable Waters and Sewage: Edward Bartow, *Chairman*; E. H. S. Bailey, H. E. Jordan, W. P. Mason, W. W. Skinner.

Committee on Nomenclature and Spelling: Editors of the Society's journals.

Committee on Occupational Diseases: Chas. Baskerville, *Chairman*; Geo. P. Adamson, H. K. Benson, Chas. E. Coates, Wm. Lloyd Evans, F. W. Frerichs, H. W. Gillett, Edward Gudeman, Milton I. Hersey, Earle B. Phelps, S. R. Scholes, F. N. Smalley.

Committee on Paper: F. P. Veitch.

Committee on Patent and Related Legislation: L. H. Baekeland, *Chairman*; Carleton Ellis, E. A. Hill, A. D. Little, C. P. Townsend, W. R. Whitney.

Committee on the Revision of Methods of Coal Sampling and Analysis (Joint with the Society for Testing Materials): W. A. Noyes, *Chairman*; Perry Barker, A. C. Fieldner, W. F. Hillebrand, A. H. White.

Committee on Code of Professional Ethics: A. D. Little, *Chairman*; L. H. Baekeland, W. D. Bancroft, Wm. Brady, F. K. Cameron.

Committee on Supervision of Chemical Engineering Catalog: Raymond F. Bacon, American Chemical Society's representative.

Supervisory Committee on Standard Methods of Analysis: W. F. Hillebrand, *Chairman*; Clifford Richardson, Geo. C. Stone, H. P. Talbot.

Membership Committee: Frank K. Cameron, *Chairman*; W. D. Bigelow, Charles L. Parsons.

Committee on Endowment: I. K. Phelps, *Chairman*; A. Lowenstein, F. R. Eldred.

Committee on Inventions by Government Employees: L. H. Baekeland, Wm. M. Grosvenor.

Perkin Medal Committee: J. M. Matthews, *Chairman*; T. B. Wagner, A. M. Comey, E. G. Love, George D. Rosengarten, M. Toch, J. C. Olsen, D. Wesson.

CHARLES L. PARSONS, *Secretary*.

#### MEMBERS ELECTED BETWEEN APRIL 15 AND MAY 15, 1916.

- Acton, Walter, 9 Trees Park Ave., Barrhead, Scotland.  
 Adams, Howard W., 409 W. Willow St., Normal, Ill.  
 Adams, Robert H., 56 Pingree Ave., Detroit, Mich.  
 Anderson, George A., 403 Emerson Ave., Syracuse, N. Y.  
 Backstrom, R., 576 Mission St., San Francisco, Calif.  
 Bates, Charles F., 712 Lodi St., Syracuse, N. Y.  
 Baumann, Louis, University Hospital, Iowa City, Ia.  
 Bent, Frank A., c/o Hercules Powder Co., Hercules, Calif.  
 Bernheim, Alice R., 148 W. 86th St., New York City.  
 Bissell, D. W., 917 W. Green St., Urbana, Ill.  
 Bodenhorn, Ellwood S., Annville, Pa.  
 Boldingh, G. Hondius, Nieuwe Presengracht 126, Amsterdam, Holland.  
 Bondy, Alfred Robert, 1266 Boston Road, New York City.  
 Bressler, J. Walter, 7147 Torresdale Ave., Philadelphia, Pa.  
 Bright, Charles G., 323 E. Doty Ave., Neenah, Wisc.  
 Brown, Alan, Hospital for Sick Children, College St., Toronto, Canada.  
 Bruce, Harry E., 433 Columbia Ave., Palmerton, Pa.  
 Churchill, Jesse Briggs, 306 Atherton St., State College, Pa.  
 Das, Premananda, Rangoon Municipality, Rangoon, India.  
 Davis, Charles Wesley, 244 Millvale Ave., E. E., Pittsburgh, Pa.  
 Davis, Horace J., 9 Myrtle St., Rochester, N. H.  
 Dixon, Henry W., Bonner Springs, Kans.  
 Eberbach, Oscar A., 831 Tappan Pl., Ann Arbor, Mich.  
 Eberhardt, L. A., 2070 Fifth Ave., New York City.  
 Einbecker, William Francis, 604 E. Springfield Ave., Champaign, Ill.  
 Ervin, Edwin A., Boothwyn, Pa.  
 Ewan, Thomas, c/o Cassel Cyanide Co., Ltd., Maryhill, Glasgow, Scotland.  
 Ferguson, Benjamin M., 5713 Calumet Ave., Chicago, Ill.  
 Fessenden, Margaret T., 46 Whitfield Rd., West Somerville, Mass.  
 Fletcher, E. Livingston, Jr., 1107 Little High St., Charlottesville, Va.  
 Forster, C. D., 357 Calle Piedras, Montevideo, Uruguay, South America.  
 Frohring, W. O., 3229 E. 93rd St., Cleveland, Ohio.  
 Goob, Gustave L., 1135 Fullerton Ave., Chicago, Ill.

- Graham, Walton C., Great Western Sugar Co., Loveland, Colo.  
 Greaves, Joseph E., Utah Experiment Station, Logan, Utah.  
 Harder, Robert C., 634 Fourth St., Port Arthur, Tex.  
 Haynes, Pierre E., 17th Floor, 42nd St. Bldg., New York City.  
 Henriques, Frederick C., 1642 Fifty-first Ave., Oakland, Calif.  
 Higgins, C. A., Union Powder Corp., Parlin, N. J.  
 Hoven, J. Roy, 6350 Sangamon St., Chicago, Ill.  
 Humphreville, R. B., 332 Valley St., Lewistown, Pa.  
 Ingvaldsen, Thorsten, 610 E. Jefferson St., Iowa City, Ia.  
 Jessop, Earle, 337 Ohio Ave., Glassport, Pa.  
 Johnson, Charles S., c/o Union Glass Co., Somerville, Mass.  
 Jones, Abner C., c/o Otis Elevator Co., Buffalo, N. Y.  
 Keegan, Harry B., 717 W. Genesee Ave., Saginaw, W. S., Mich  
 Keyzer, Fred A., 82 Farragut Rd., Swampscott, Mass.  
 King, Kenneth T., Rothschild, Wisc.  
 Kingsley, E. D., 18 East 41st St., New York City.  
 Kroh, Stephen J., Moscow, Idaho.  
 Landis, Maurice Neuman, 3800 Grand Blvd., Chicago, Ill.  
 Lederer, F. B., 6 South Warren St., Madison, Wisc.  
 Lewis, M. Smyser, 117 S. Eastern Ave., Joliet, Ill.  
 Locke, F. L., 17 Union Ave., Crafton, Pa.  
 Loose, Kenneth David. Loose-Wiles Biscuit Co., Long Island City,  
 N. Y.  
 Lowenstein, Herman H., 1902 West End Ave., Nashville, Tenn.  
 McMillen, Walter W., Morenci, Ariz.  
 McKenzie, Kenneth Cisco, 1414 Watchung Ave., Plainfield, N. J.  
 Mack, George R. T., Downs Bldg., Seattle, Wash.  
 Marshall, Warren G., Hakalau, Hawaii, T. H.  
 Mast, Clarence S., 530 W. Latimer St., Abingdon, Ill.  
 Matthews, Corwin, 224 Millvale Ave., Pittsburgh, Pa.  
 Maurer, Siegfried, Anatomy Bldg., University of Chicago, Chicago, Ill.  
 Minaeff, M., c/o Union Powder Corp., Parlin, N. J.  
 Misumi, Aizo, Asahi Glass Co., Tsurumi near Yokohama, Japan.  
 Murray, Victor Feodor, Fuel Testing Plant, Cor. Plymouth and Booth  
 Sts., Ottawa, Canada.  
 Nakatani, Shuzo, c/o Dr. S. W. Miller, 1273 Vine St., Denver, Colo.  
 Paquet, F., Marmora, Ontario, Canada.  
 Payne, Anne MacGregor, 317 Outlook Bldg., Columbus, Ohio.  
 Persoon, Hubertus Jacobus, N. Bueno Vista Ave., Yonkers, N. Y.  
 Picker, Alfred R., 2322 Olive St., St. Louis, Mo.  
 Putnam, A. H., Box 486, Ilion, N. Y.  
 Quaintance, Chas. F., Golden, Colo.  
 Read, L. C., 1210 Union Oil Bldg., Los Angeles, Calif.  
 Redman, S. L., 460 E. Ohio St., Chicago, Ill.  
 Rice, S. A., 1323 Dace Ave., Sioux City, Iowa.  
 Rodenbaugh, Frederick Hase, Hooper Institute for Medical Research,  
 University of California, San Francisco Calif.  
 Ross, Wm. Wrighton Eustace, Georgetown, Ontario, Canada.  
 Royer, Charles, 1 Ernest St., Maisonneuve, Montreal, Canada.  
 Schad, Frank M., c/o E. R. Squibb & Sons, Brooklyn, N. Y.  
 Scott, Clarence L., Box 333, Altoona, Pa.

Scott, John T., Indiana Laboratories Co., Hammond, Ind.  
 Shaffer, Earl W., 405 West California Ave., Urbana, Ill.  
 Shohl, Alfred Theodore, 105 Jackson Place, Baltimore, Md.  
 Siefert, H. G., Box 202, Altadena, Calif.  
 Slippery, Horace A., Box 92, Newton, Kans.  
 Smith, Charles Russell, 48 Shawmist St., Lewiston, Maine.  
 Smith, E. Bernard, 164 McGregor Ave., Sault Ste. Marie, Ont., Canada.  
 Strickler, A., 220 Pearl St., Ypsilanti, Mich.  
 Talcott, Avis, Department of Chemistry, Kansas University, Lawrence, Kans.  
 Thomas, M. D., Lincoln College, Oxford, England.  
 Thorp, Gerald, St. Elmo Club, South Bethlehem, Pa.  
 Thurston, Allen M., Du Pont Hotel, City Point, Va.  
 Turner, Wendell P., 13 School St., Springfield, Mass.  
 Wachter, Louis E., 2015 Palmetto St., Brooklyn, N. Y.  
 Washburn, Earl M., 712 Lodi St., Syracuse, N. Y.  
 Weitbrecht, George, 320 Orange Ave., Santa Ana, Calif.  
 Welsh, William Thomas, 316 Main Bldg., State College, Pa.  
 White, Albert E., 1220 Prospect St., Ann Arbor, Mich.  
 Wolstoncroft, Irvin C., Box 16, McKees Rocks, Pa.  
 Wood, Burton G., Thompsonville, Mich.  
 Zurcher, Paul, Warner House, Emporium, Pa.

#### CORPORATION MEMBER.

The Pfaudler Co., 217 Cutler Bldg., Rochester, N. Y.

### MEETINGS OF THE SECTIONS.

[Full accounts of all meetings should be sent to Secretary Charles L. Parsons, Box 505, Washington, D. C.]

#### ALABAMA SECTION.

The May meeting was held May 6th. Dr. Clarence N. Wiley read a paper on, "The Role of the Chemist in the Cement Industry." The retiring President, Dr. Stewart J. Lloyd, gave a talk on "Isotopic Elements." Prof. B. B. Ross, who is the Alabama member of the National Committee on Preparedness, told of the purpose of his committee and asked coöperation of every member.

The officers for the ensuing year were elected as follows: *President*, A. H. Olive; *First Vice-President*, J. P. Montgomery; *Second Vice-President*, C. N. Wiley; *Secretary-Treasurer*, Wm. H. Beers, Jr.; *Councilor*, 1916, Stewart J. Lloyd.

WM. H. BEERS, JR., *Secretary*.

#### SOUTH DAKOTA SECTION.

The Section met in its organization meeting on May 6th. The following program was given: "The Free Energy of Dilution of Sulfuric Acid," by Orville E. Cushman and Merle Randall; "A Study of Canned Salmon, A Preliminary Note," by Cecil Clemens and Sylvanna Elliott; "A Modified Scheme for Qualitative Analysis," by O. R. Overman; "The Nitro Phenyl

Ethers," by Hilton Ira Jones and Alfred N. Cook; "Some Subjects under Investigation in The Chemical Laboratories of the University of South Dakota," by Alfred N. Cook.

The following officers were elected: *President*, Alfred N. Cook; *Vice-President*, B. A. Dunbar; *Secretary*, H. I. Jones; *Treasurer*, H. F. Hadley; *Councilor*, O. R. Overman.

HILTON IRA JONES, *Secretary*.

#### MILWAUKEE SECTION.

The April meeting was held the 21st. Mr. C. J. Atkinson, Metallurgical Engineer, gave a lecture, illustrated by lantern slides, on the "Metallography of Iron and Steel."

A meeting was held May 10th. Dr. H. E. Horton of the American Steel & Wire Co., Chicago, gave a lecture entitled: "Through the Furnace to the Farm."

H. T. McALLISTER, *Secretary*.

#### NORTHERN INTERMOUNTAIN SECTION.

The Section held its annual meeting May 6th. Program: "Two Methods for the Separation of the Alkaline Earth Group," by Professor Alice G. Paterson; "Recent Advances in Ore-Dressing," by Dr. R. R. Goodrich; "Composition and Baking Value of Dry Farmed and Irrigated Wheat," by Professor J. S. Jones; "Electric Laboratory Heating Device," by Harry Redekey Rupert.

The following were elected as officers for 1916: Professor Carl M. Brewster, *Chairman*; Dr. John A. Kostalek, *Vice-Chairman*; Professor Geo. A. Olson, *Councilor*; Professor H. A. Holaday, *Secretary-Treasurer*.

GEO. A. OLSON, *Secretary*.

#### INDIANA SECTION.

A meeting was held April 21st. Dr. Chas. H. Herty delivered an address on "Chemistry as an Aid to the Efficiency of Democracy."

The regular meeting was held May 13th. Program: "Detection of Nickel and Cobalt Salts," by A. R. Middleton; "Nonprotein Forms of Nitrogen in Alfalfa," by R. H. Carr; "Electromotive-Force Measurements with Tenth Normal Hydrochloric Acid and Calomel Electrodes," by N. E. Loomis.

H. W. RHODEHAMEL, *Secretary*.

#### COLUMBUS SECTION.

The May meeting was held May 5th. Program: "Rate of Absorption of CO<sub>2</sub> by Soda-lime," by Professor C. W. Foulk; "Determination of Transition Points by Difference of Potential Methods," by Mr. I. M. Geiger.

Review of the Urbana meeting of the American Chemical Society, Mr. E. J. Crane; Professor G. O. Higley, Ohio Wesleyan; Professor Wm. E. Henderson; Professor James E. Withrow.

WM. J. McCaUGHEY, *Secretary*.

## CALIFORNIA SECTION.

The ninety-first regular meeting was held April 15th. Program: "Borax and Its Uses," by Mr. T. M. Cramer, Superintendent, Pacific Coast Borax Company; "The Chemistry of Copper Ore Enrichment," by Professor S. W. Young, of Stanford University.

On May 2nd there was held a joint meeting on military preparedness.

*San Francisco Sections:* American Chemical Society; American Institute of Electrical Engineers; American Society of Mechanical Engineers; American Institute of Mining Engineers; American Society of Civil Engineers.

Three papers were presented: "Methods by Which the Civilian Engineers Can Prepare Themselves to Assist the Engineer Corps of the U. S. Army in Case of War," by Capt. Richard Park, Engineer Corps, U. S. A.; "The Work at the Military Training Camps," by Capt. John Murphy, Coast Artillery, U. S. A.; "An Outline of the Work of the Organization for Industrial Preparedness of the Naval Consulting Board," by A. H. Babcock, Member of the Naval Consulting Board.

BRYANT S. DRAKE, *Secretary*.

## PITTSBURGH SECTION.

The 126th regular meeting of the Section was held April 20th. Program: "Constitution of Porcelains," by A. A. Klein; "Manufacture of Table Glass Ware," by S. R. Scholes.

W. C. COPE, *Secretary*.

## ST. LOUIS SECTION.

The regular meeting was held April 4th. Program: Mr. W. C. Hamilton, Chief Chemist of the American Steel Foundry, addressed the Section on, "Modern Methods in the Manufacture of Steel Castings."

The May meeting was held May 1st. Program: "The Biological Chemistry of the Colon Group," by Dr. Frederick A. Baldwin.

GEO. LANG, JR., *Secretary*.

## NORTH CAROLINA SECTION.

The spring meeting was held April 29th.

The following officers were elected for the ensuing year: *President*, Dr. J. K. Plummer, Raleigh, N. C.; *Vice-President*, Dr. H. B. Arbuckle, Davidson, N. C.; *Secretary-Treasurer*, F. E. Carruth, West Raleigh, N. C.; *Councilor*, Dr. A. S. Wheeler, Chapel Hill, N. C.; *Reporter*, L. B. Rhodes, Raleigh, N. C.

The following papers were presented: "The Action of Ammonia on Arsenic Iodide," by Dr. Chas. H. Herty and C. B. Carter; "Some Properties of the Solutions of Substantive Cotton Dyes," by F. E. Carruth; "Electrolysis of Certain Inorganic Salts in Liquid Ammonia Solution,"



by C. F. Miller; "The Chemistry of Gossypol," by Prof. W. A. Withers and F. E. Carruth.

J. T. DOBBINS, *Secretary*.

#### IOWA SECTION.

The annual meeting was held Saturday April 29. Program: "Electromotive Forces and Electrode Potentials in Pure and Mixed Solvents. II," by F. S. Mortimore and J. N. Pearce; "Barium in Tobacco," by Nicholas Knight; "Pure Sodium Chloride," by Nicholas Knight; "Acid Potassium and Sodium Phthalates as Standards in Acidimetry and Alkalimetry" (Second Paper), by W. S. Hendrixson; "An Improved Method of Solubility Determination," by W. S. Hendrixson; "Auxo-amylases," by E. W. Rockwood; "Conditions Existing in Solutions near the Critical Temperature" (a preliminary paper), by P. A. Bond.

By invitation the following papers were read: "A Comparison of Barbituric Acid, Thiobarbituric Acid and Malonylguanidine as Quantitative Precipitants for Furfural," by A. W. Dox and G. P. Plaisance, Agricultural Experiment Station, State College; "An Accurate Aeration Method for Determining Alcohol in Fermentation Mixtures," by A. W. Dox and A. R. Lamb, Agricultural Experiment Station, State College; "Relative Influence of Bacteria and Enzymes on Silage Fermentation," Preliminary Report, by A. R. Lamb, Agricultural Experiment Station, State College; "Estimation of Calcium in Ash of Forage Plants and Animal Carcasses," by S. B. Kuzirian, Agricultural Experiment Station, State College.

P. A. BOND, *Secretary*.

#### WISCONSIN SECTION.

The April meeting was held April 26th. Professor O. L. Kowalke spoke on "Some Characteristics of Base Metal Thermocouples."

The May meeting was held May 10th. Prof. M. A. Rosanoff, of Mellon Institute, spoke on "The Theory of Distillation."

L. F. AUGSPURGER, *Secretary*.

#### ROCHESTER SECTION.

A meeting was held May 1st. Dr. W. R. White of the Geophysical Laboratory, Washington, D. C., gave a talk on "The Development of Calorimetry."

A meeting was held May 15th. Program: Mr. H. Y. Norwood of the Taylor Instrument Companies gave a talk on "The Mercurial Thermometer and its Adaption to Industrial Arts."

H. H. TOZIER, *Secretary*.

#### LOUISIANA SECTION.

The 94th meeting was held April 21st. Program: "A Preliminary Report on Raw Materials Available for Certain Louisiana Chemical Industries, by the Committee on Resources," by Dr. Chas. E. Coates, *Chairman*.

F. W. LIEPNER, *Secretary*.

## UNIVERSITY OF MICHIGAN SECTION.

The April meeting was held April 27th. Dr. Oliver Kamm gave a paper on "Some Relationships between Ionization and Structure in Unsaturated Acids."

H. H. WILLARD, *Secretary*.

## NEW HAVEN SECTION.

A meeting was held April 14th. Dr. B. C. Hesse addressed the Section on "The Experimental Methods of the Badische Anilin and Soda Fabrik."

GEORGE S. JAMIESON, *Secretary*.

## DETROIT SECTION.

The 80th regular meeting was held April 15th. Program: Dr. H. P. Talbot, Dean of Chemistry and Chemical Engineering of the Mass. Institute of Technology, lectured on "The Rare Gases."

The 81st regular meeting was held May 18th. Program: "Modern Facts on Cider Vinegar," by Floyd W. Robison.

EDWARD J. GUTSCHE, *Secretary*.

## SYRACUSE SECTION.

The 106th regular meeting was held April 21st. Program: "The Flow of Heat through Furnace Walls. Radiation of Heat from Furnaces. Proper Materials to be Used in the Making of Mortar for Use in Furnaces," by Prof. J. W. Richard.

R. S. BOENNER, *Secretary*.

## CHICAGO SECTION.

The regular meeting was held May 19th. At this meeting the Willard Gibbs Medal was presented to Dr. W. R. Whitney. The following officers were elected to serve for the ensuing year: A. V. H. Mory, *Chairman*; C. S. Miner, *First Vice-Chairman*; C. A. Tibbals, Jr., *Second Vice-Chairman*; D. K. French, *Secretary-Treasurer*; A. Lowenstein, L. M. Tolman, A. M. Taylor, W. R. Smith, Wm. Brady, H. N. McCoy, *Councilors* for 1917.

D. K. FRENCH, *Secretary*.

## NEW YORK SECTION.

The 6th regular meeting of the session 1915-16 was held April 7th. Program: "University and Industry," by William H. Nichols, B.S., M.S., LL.D., Sc.D. Discussion by Marston T. Bogert, Columbia University; Elon H. Hooker, Hooker Electrochemical Company; Phoebus A. Levene, The Rockefeller Institute for Medical Research; Benjamin L. Murray, Merck & Company.

C. M. JOYCE, *Secretary*.

## EASTERN NEW YORK SECTION.

The 65th meeting was held April 7th. Dr. H. B. Goodrich lectured on "The Mendelian Theory of Heredity and the Determination of Sex" (illustrated).

The 66th regular meeting was held May 2nd. Program: Subject: "Calorimetry: The Development of Calorimetry," by Dr. W. P. White, Geophysical Laboratory, Washington, D. C. *ALBERT J. SALATHE, Secretary.*

#### WESTERN NEW YORK SECTION.

At the regular meeting, March 23rd, Dr. K. F. Stahl spoke on "Hydrofluoric Acid and Fluorides."

On April 4th a joint meeting was held with Niagara Falls Section, American Electrochemical Society. Dr. Robert B. Sosman, of the Geophysical Laboratory, Carnegie Institution of Washington, spoke on "The Common Refractory Oxides."

*R. H. WHITE, Secretary.*

#### PHILADELPHIA SECTION.

The regular meeting was held May 18th. Program: "The Manufacture of Vaccines and Serums," by C. W. Brown.

*J. HOWARD GRAHAM, Secretary.*

#### LEXINGTON SECTION.

The 33rd regular meeting was held May 11th. Program: "Note on the Occurrence of Gallium," by Dr. R. N. Maxson; "The Growth of Isolated Plant Embryos," by Dr. G. D. Buckner; "On the Reaction between Iodine and Tetrathionate," by Dr. P. L. Blumenthal.

*P. L. BLUMENTHAL, Secretary.*

#### CLEVELAND SECTION.

The May meeting was held in the Chemical Laboratory of Case School of Applied Science May 8th. Prof. C. F. Mabery addressed the Society on "The Relations in Origin and Composition of Coal, Petroleum and the Natural Asphalts."

*A. F. O. GERMANN, Secretary.*

#### WASHINGTON SECTION.

The 261st meeting was held May 11th. Program: "The Preparation of Heavy Metal Salts of Certain Organic Acids," by C. N. Myers, Hygienic Laboratory; "Some Observations upon the Toxicity and Chemotherapy of the Heavy Metals," by G. C. Lake, Hygienic Laboratory; "The Separation and Determination of Small Amounts of Antimony," by Elias Elvove, Hygienic Laboratory.

*E. C. McKEIVY, Secretary.*

#### OREGON SECTION.

The 28th regular meeting was held May 6th. Prof. A. A. Knowlton, of Reed College, presented a paper on "The Synthesis of Metals."

*NORMAN C. THORNE, Secretary.*

## MARYLAND SECTION.

The 14th regular meeting was held May 13th. Program: "Measurement of Osmotic Pressure of Concentrated Sugar Solutions," by R. T. Myrick; "Esterification of Acids by Mercaptans," by J. H. Sachs and J. W. Kimball; "Catalytic Preparation of Nitriles," by G. D. Van Epps; "The Identification of Acids," by J. A. Lyman and E. Emmet Reid; "The Manufacture of Ethyl Alcohol," by H. W. Berger.

FRANK M. BOYLES, *Secretary*.

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## DECEASED.

Turner, Herbert S., Oglesby, Ill., died April, 1916.

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# Proceedings.

## COUNCIL.

MEMBERS ELECTED BETWEEN MAY 15 AND JUNE 15, 1916.

- Appel, Maurice, 9 East 38th St., Bayonne, N. J.  
Bashore, E. G., La Tourette Hotel, Bayonne, N. J.  
Belfit, Robert W., 785 North St., Pittsfield, Mass.  
Berger, Emily V., 1602 Louisiana St., Lawrence, Kans.  
Blakemore, Herbert S., Lewiston, Calif.  
Boyce, T. D., Bakersfield, Calif.  
Brede, L. H., 414 N. Morrison Ave., Collinsville, Ill.  
Bridgeman, Oscar C., University of Saskatchewan, Saskatoon, Sask., Canada.  
Brown, Frank E., Jr., 923 So. Jefferson St., Roanoke, Va.  
Buck, Harry C., 3307 N. Broad St., Philadelphia, Pa.  
Clark, O. E., West Middlesex, Pa.  
Cohen, William H., International Correspondence Schools, Scranton, Pa.  
Davies, Emlyn, Nicholson, Pa.  
Delp, Wm. S., 2120 N. Third St., Philadelphia, Pa.  
Drinker, Philip H., South Bethlehem, Pa.  
Essex, Jesse L., 523 Russell St., W. Lafayette, Ind.  
Foresman, G. K., 110 South Ninth St., Lafayette, Ind.  
Garrett, C. Scott, H. M. Factory, Dean Forest, near Coleford, Glos., England.  
Hansen, Clarence T., 43 Fayette St., Cambridge, Mass.  
Hargreaves, Frank, Hough Green, Widnes, England.  
Harrington, William J., General Delivery, Hibbing, Minn.  
Henius, E. T., 1135 Fullerton Ave., Chicago, Ill.  
Herman, Ralph S., Ismert-Hincke Milling Co., Kansas City, Kans.  
Hubel, Jesse H., 112 West Alexandrine Ave., Detroit, Mich.  
Jeffery, Joseph A., Jeffery-Dewitt Co., Butler Ave. & G. T. R. R., Detroit, Mich.  
Jones, Owen B., 19 Hampden Hall, Cambridge, Mass.  
Kearney, John J., 6433 Fairfield Ave., Berwyn, Ill.  
Kearsley, Edward, Room 633, Y. M. C. A., Halsey St., Newark, N. J.  
Kenly, Charles E., Emporium, Pa.  
Klein, Carl A., 4 Brimsdown Ave., Enfield Highway, Middlesex, England.  
Klein, Leonard, University of Arizona, Tucson, Ariz.  
Leiss, Paul E., 465 West Dewey Ave., Youngstown, Ohio.  
Linhart, Geo. A., Chem. Annex, Univ. of California, Berkeley, Calif.  
Lucast, Edmund, 118 James St., Waukesha, Wis.  
Lyder, E. E., Empire Gas & Fuel Co., Bartlesville, Okla.  
MacDonald, A. D., 127 Mt. Auburn St., Cambridge, Mass.  
Mahoney, Frank H., 112 Ocean St., Dorchester, Mass.  
Martinez, John M., 82 Beaver St., New York City.  
McRoberts, D. C., Apt. 2, 69 Layman Ave., Indianapolis, Ind.  
Milligan, Lowell H., 301 W. 6th Ave., Columbus, Ohio.

- Mumford, Nicholas V. S., 50 Humboldt Ave., Providence, R. I.  
 Nelson, Victor E., Dept. of Agricultural Chemistry, Madison, Wis.  
 Petty, Clarence L., 1200 Sixteenth St., Altoona, Pa.  
 Rector, Thomas M., Pompeian Co., Coca Cola Bldg., Baltimore, Md.  
 Robinson, T. H., Lawrenceville, N. J.  
 Rose, Robert E., 4723 Thackeray Place, Seattle, Wash.  
 Santos, Jose M., 561 Middle St., Baton Rouge, La.  
 Seamon, W. H., Jr., Gage, New Mex.  
 Simpson, G. E., Western Reserve Medical School, Cleveland, Ohio.  
 Smith, C. C., Riverside Club House, Pennsgrove, N. J.  
 Steineck, Frank E., 3210 Arthington St., Chicago, Ill.  
 Sundstrom, Hans, c/o Universal Portland Cement Co., New Duluth, Minn.  
 Thompson, Lemuel H., 5 Washington Pl., Morristown, N. J.  
 Tsiropinas, Fedon, 200 Pleasant St., Milwaukee, Wis.  
 Walker, Charles R., Box 912, Kingston, N. Y.  
 Walter, George A., Watkins, N. Y.  
 Ward, Henry L., 146 S. Hamlin Ave., Chicago, Ill.  
 Ward, Nell M., 2500 Garfield St., Lincoln, Nebr.  
 White, L. K., Sapulpa, Okla.  
 Wiseman, Harry O., 1789 Ogden Ave., Chicago, Ill.  
 Zimmerman, Oliver B., 324 So. Ashland Ave., La Grange, Ill.  
 Zinn, John B., 2 Tyler Place, Amherst, Mass.

CORPORATION MEMBER.

Federal Dyestuff & Chemical Co., Kingsport, Tenn.

## MEETINGS OF THE SECTIONS.

[Full accounts of all meetings should be sent to Secretary Charles L. Parsons, Box 505, Washington, D. C.]

### INDIANA SECTION.

The last meeting of this year was held June 9. Program: "Theory and Practice of Making Serums and Vaccines," by Dr. Severance Burgence.

H. W. RHODEHAMEL, *Secretary*.

### ST. LOUIS SECTION.

The Section met June 5. Mr. Edward Mallinckrodt, Jr., read a paper on "The Determination of Water and Alcohol in Ether."

GEO. LANG, JR., *Secretary*.

### KANSAS CITY SECTION.

The 117th meeting of the Kansas City Section was held April 29. An illustrated lecture on "Ancient Chemistry" was given by Professor F. B. Dains.

The 118th meeting was held May 20. Program: "The Chemical Conditions Necessary for Making Alfalfa Silage," C. O. Swanson. "Notes on New and Non-official Remedies and the Propaganda of Reform,"

R. H. Needham. "On the Nutritional Deficiencies of Corn," J. T. Willard.

W. B. SMITH, *Secretary*.

#### EASTERN NEW YORK SECTION.

The 67th regular meeting of the Section was held in Amsterdam June 3. Program: "Manufacture and Uses of Linseed Products," by A. C. Goetz. "The Dye Situation," by Aug. Amrein.

ALBERT J. SALATHE, *Secretary*.

#### NEW YORK SECTION

The 7th regular meeting of the session of 1915-16 was held on May 19 in conjunction with the New York Sections of the American Electrochemical Society and the Society of Chemical Industry, under the auspices of the latter society. Program: "Some Problems in the Petroleum Industry," by Dr. Raymond F. Baker.

The eighth regular meeting of the session of 1915-16 was held June 9. Program: "An Account of Some Experiments Relating to Vapor Pressures, Fractional Distillation, Critical Data and Compressibility of Gases," by George A. Burrell. "The Petrographic Microscope in Analysis," by Frederick E. Wright.

C. M. JOYCE, *Secretary*.

#### NASHVILLE SECTION.

The 41st meeting was held May 19. The program included the following papers: "Studies in Preservation of Diphtherial Toxin, for Schlick's Test," by Dr. Wm. Litterer.

The following officers were elected: J. F. Norris, *Chairman*; W. H. Hollinshead, *Vice-Chairman*; Paul C. Bowers, *Sec.-Treas.*; J. I. D. Hinds, *Councilor*.

PAUL C. BOWERS, *Secretary*.

#### WASHINGTON SECTION.

A joint meeting of the Society of Engineers and this Section was held May 24. Program: "The Machine Shop and the Chemical Laboratory as Related to National Preparedness for Defense," by Mr. Joseph Steinmetz, President of the Aero Club of Pennsylvania.

E. C. MCKELVY, *Secretary*.

#### CINCINNATI SECTION.

The 206th regular meeting was held May 17. Program: "Milk Clarifiers," by Clarence Bahlmann.

E. K. FILES, *Secretary*.

#### UNIVERSITY OF MICHIGAN SECTION.

The May meeting of the Section of the American Chemical Society was held May 23. Mr. C. S. Schoepfle presented a paper on "The Molecular Weights of Free Radicals."

H. H. WILLARD, *Secretary*.

## NEBRASKA SECTION.

The May meeting was held May 27. Program: "Some Substances Essential to Growth," by John W. Calvin. "Life and Work of Professor J. U. Neff," by Dr. F. W. Upson.

H. M. PLUM, *Secretary*.

## PITTSBURGH SECTION.

A special meeting of the Section was held May 25. Program: "Smelter Smoke and Arsenical Poisoning," by W. D. Harkins, Professor of Chemistry, University of Chicago and Chairman of the Chicago Section of the American Chemical Society.

The 128th regular meeting was held June 15. Program: "Chemistry and the Present War: How It May Affect the Future of the Chemical Industries in the United States," by L. H. Baekeland.

W. C. COPE, *Secretary*.

## LOUISIANA SECTION.

The 96th meeting was held June 16. Program: "The Estimation of Minute Quantities of Sulfur Dioxide in the Atmosphere," by C. S. Williamson, Jr. "Notes on the Analysis of Aspirin," by C. L. Clay.

F. W. LIEPNER, *Secretary*.

## CORNELL SECTION.

The regular meeting was held May 23. Program: "Some Topics in Luminescence," by Prof. E. L. Nichols.

J. A. BRIDGMAN, *Secretary*.

## CLEVELAND SECTION.

A special meeting was held June 16, in connection with the eighth semi-annual meeting of the American Institute of Chemical Engineers. The following papers were presented: "Water Powers of the United States," by Herman Stabler, Chemist and Engineer, U. S. Geological Survey; "Acid Resisting Alloys," by W. C. Carnell.

A. F. O. GERMANN, *Secretary*.

## ROCHESTER SECTION.

At the annual meeting, held on May 15, the following officers were elected to serve for the ensuing year: *Chairman*, C. F. Hutchison; *Vice-Chairman*, R. F. Baxter; *Sec.-Treas.*, H. H. Tozier.

H. H. TOZIER, *Secretary*.

## CHICAGO SECTION.

The June meeting was held June 7. Dr. B. C. Hesse addressed the Section on "Our Responsibilities."

D. K. FRENCH, *Secretary*.

## VERMONT SECTION.

At its organization meeting on May 19, the following officers were elected: *Chairman*, S. F. Howard; *Vice-Chairman*, P. C. Voter; *Sec.-Treas.*, C. E. Burke; *Councilor*, 1916, G. H. Burrows.

C. E. BURKE, *Secretary*.



## DETROIT SECTION.

The following officers were elected at the meeting on May 18: Howard T. Graber, *Pres.*; Edw. J. Gutsche, *Vice-Pres.*; James H. Bogart, *Sec.*; E. E. Follin, *Treasurer*.

EDW. J. GUTSCHE, *Secretary*.

## NEW HAVEN SECTION.

The regular meeting was held May 19. Professor Charles A. Kraus, of Clark University, gave a lecture, with demonstrations, on "Some Recent Developments in Glasses and the Art of Glass Blowing."

GEORGE S. JAMIESON, *Secretary*.

## UNIVERSITY OF ILLINOIS SECTION.

The regular meeting was held May 23. Program: "A Theory of the Formation of Smooth Deposits by Electrolysis," by Dr. A. MacInnes and R. W. Morgan. "The Contamination of Precipitates," by G. McP. Smith.

G. D. BRAL, *Secretary*.

## SYRACUSE SECTION.

The 107th regular meeting of the Section was held June 2. Dr. E. C. Sullivan, of the Corning Glass Works, addressed the Section on "Some Phases of Glass Manufacture."

R. S. BORNHNER, *Secretary*.

## PUGET SOUND SECTION.

The May meeting was a joint meeting with the Lumbermen's Association held May 27. Dr. Benson presented a paper on, "By-Products of the Lumber Industry," based upon his work with the Federal Bureau.

H. L. TRUMBULL, *Secretary*.

## VAN'T HOFF FUND.

According to the regulations of the van't Hoff Fund, founded June 28, 1913, interested persons are sent the following information:

The foundation, with headquarters at Amsterdam, is under the supervision of the Royal Academy of Sciences, and grants each year, before the 1st of March, from the income of the fund, certain sums to investigators in the field of pure and applied chemistry who have applied for same before November 1st of the previous year. At the present time the Committee in charge of the fund consists of A. F. Holleman (*President*), S. Hoogewerff, A. Smits, E. H. Buchner (*Secretary*), to whom applications should be addressed. The Committee has the privilege of enlarging its membership by the appointment of others for one-year terms.

The names of grantees will be published. Any individuals who have received a grant are expected to send to the Committee copies of papers relating to the results of their work, but they are otherwise at liberty to choose the manner and place of publication, with the simple requirement

that they mention the fact that the research was made from an endowment received under the van't Hoff Fund. The amount available for 1917 will be approximately \$520.

Application should be sent, registered by post, to: Het Bestuur der Koninklyke Akademie van Wetenschappen; bestemd Voor de Commissie van het "van't Hoff fonds," Trippenhuis, Kloveniersburgwal, te Amsterdam, with a detailed account of the proposed use of the grant, and of the reasons on which the candidates ground their claim. They must be received before November 1, 1916.

In the name of the Committee of the "*van't Hoff Fund*."

A. F. HOLLEMAN, *President*.

E. H. BUCHNER, *Secretary*.

Amsterdam, the month of May, 1916.

### Harry Clary Jones.

Harry Clary Jones, Professor of Physical Chemistry in Johns Hopkins University, died suddenly on April 9th last, in the fifty-first year of his age. He was born at New London, Maryland, where his father was a prosperous farmer. His early life was spent at home where the educational advantages were not of the best. In spite of the handicap he prepared himself for higher work and in 1885, when he was 20 years old, he was admitted to the Johns Hopkins University as a "special student," his preparation not having been sufficient to enable him to pass all the entrance examinations. In a short time, however, he was received as a regular candidate for the degree of bachelor of arts and this degree was conferred upon him in 1889. The traits which became so conspicuous in his later years were clearly exhibited in his undergraduate life—untiring industry, intellectual alertness, and the power of acquisition. He was a marked man from the beginning of his career as a student.

His interest in physical science was awakened by reading one of Tyndall's books that were so popular a generation ago, and it was in this way that he was led to college doors. He had to work hard before they were opened wide enough to permit of his entrance, but hard work was his specialty.

After receiving the bachelor's degree he continued his studies, devoting himself largely to chemistry, physics, and mathematics. In the third year of his graduate work he was selected as one of the Fellows of the university, which is good evidence of the esteem in which he was held by his teachers. His introduction to research was made under Professor H. N. Morse with whom he carried out two pieces of work, one "On the Action of Metallic Cadmium on the Halogen Salts of Cadmium and on the Sub-hydroxide and Sub-oxide of Cadmium" and the other on "A Redetermination of the Atomic Weight of Cadmium."

In 1892 he received the degree of Doctor of Philosophy from the Johns Hopkins University. At that time the subject of physical chemistry had come into great prominence in consequence of the work of van't Hoff, of Ostwald, and of Arrhenius. Jones was attracted to this field and determined to go abroad for the purpose of studying with these three leaders. He went first to Leipsic where he came under the influence of Ostwald; then to Stockholm to be with Arrhenius; and then to Amsterdam to sit at the feet of that genius, the genial van't Hoff. Two years were spent in this way and during this time Jones became an out-and-out physical chemist. His intense way of doing things and of looking at things led him to certain scientific excesses which jarred somewhat on the feelings of conservatives, but his tremendous enthusiasm and energy offset these defects.

The year after his return from Europe he held the position of Fellow by Courtesy in the Johns Hopkins University. This was a purely honorary position. He taught a little and carried on investigations. The next year, 1895, he was appointed Instructor in Physical Chemistry and began his career as a regular teacher of his favorite subject in his *Alma Mater*. In 1898 he was promoted to the position of Associate. In 1900 he became Associate Professor; and in 1903 Professor, which position he held at the time of his death.

During his entire career research was a passion with him and few chemists in a period of twenty years have contributed a larger number of memoirs to the literature of their subject. But this was not enough for him. He also wrote a number of books—text-books of inorganic chemistry and of physical chemistry, and treatises on special chapters of physical chemistry, some of these of a semi-popular nature.

His researches had their inception in the laboratory of Arrhenius where he began the work on the hydrates of sulfuric acid. Shortly after his return to this country he took up a systematic inquiry into the reasons for the failure of other than ideal solutions to conform to the laws of gas pressure and the theory of electrolytic dissociation, and in 1903 he was enabled to enlarge the scope of his work by the aid of generous grants from the Carnegie Institution of Washington which were continued up to the time of his death.

His earlier work was devoted to a study of the abnormalities in the molecular depression of the freezing point shown by certain substances having water of crystallization. In 1900 he offered the following tentative explanation: "In concentrated solutions these substances must take up a part of the water forming complex compounds with it and thus removing it from the field of action as far as freezing-point lowering is concerned. . . . . The lowering of the freezing point is thus abnormally great, because a part of the water is no longer present as solvent. . . . .

We do not put forward the above suggestion as the final statement of a theory, but only as a tentative explanation which, however, seems to account for the experimental facts which have been brought to light." This is the first appearance of his hydrate theory which was the guiding thought in all his subsequent experimental work.

About 1901 another line of investigation was opened up—the study of the conductivity and dissociation of electrolytes and their temperature coefficients; and, a little later, work on the absorption spectra of solutions was begun.

Using the conductivity method, a study of a large number of inorganic compounds and of organic acids was made in water alone. This work was soon extended to non-aqueous and mixed solvents and, in this connection, parallel investigations on the viscosity of the solutions were carried out and the important bearing of this property upon conductance established, as well as the explanation of certain phenomena, *e. g.*, negative viscosity coefficients.

The last phase of his work was the study of the absorption spectra of solutions and their bearing on solvation. This involved observations on thousands of solutions. Four of the ten monographs embodying the results of his investigations carried out under the auspices of the Carnegie Institution of Washington were devoted to a discussion of the results obtained both in aqueous and non-aqueous solutions. The most recent work was carried out with a fine grating spectroscope and radiomicrometer combined. With this not only were the phenomena of solvation investigated, but the ionization constants of indicators and the light absorption coefficients of solutions as well.

Space will not permit a discussion of the wide application of the results obtained from these various lines of investigation followed by Professor Jones and his students, but fortunately we have such a discussion in his own words in Chapter VII, *Publication 210*, Carnegie Institution of Washington as well as a complete bibliography up to 1915 of all his publications on the solvate theory. A quotation from his writings may be employed to give his own estimate of the place of the theory in chemistry. He says: "The theory of electrolytic dissociation, supplemented by the theory of solvation, is then not simply a theory of dilute or ideal solutions, but a theory of solutions in general."

Chemistry has lost one of her most industrious, most energetic, and most enthusiastic devotees.

IRA REMSEN.

# Proceedings.

## COUNCIL.

President Herty has appointed the following to represent the Society in coöperating with the National Academy of Sciences on Nitrate Supply for the United States Government: Chas. H. Herty, W. R. Whitney, Leo H. Baekeland, and W. K. Lewis.

### MEMBERS ELECTED BETWEEN JUNE 15 AND JULY 15, 1916.

- Babcock, J. H., Institute of Industrial Research, Washington, D. C.  
Bantrell, M. A., 206 Meigs St., Rochester, N. Y.  
Bauer, Edward A., 2034 N. Crawford Ave., Chicago, Ill.  
Bayliss, William, Y. M. C. A., Muncie, Ind.  
Bower, Leibert W., Eagle Mills, Arkansas.  
Breese, Kenneth E., Grand Mere, P. Q., Canada.  
Brodsky, Israel J., 5118 Parkside Ave., Philadelphia, Pa.  
Broggini, Mario J., 1475 Coutant St., Lakewood, Ohio.  
Brown, Norman B., Shawinigan Falls, Quebec, Canada.  
Buchanan, Ruth, 423 S. Graham St., Pittsburgh, Pa.  
Birmingham, Foster A., 1118 Burns Ave., St. Paul, Minn.  
Coolidge, Albert Sprague, Pittsfield, Mass.  
Davis, N. W., 3820 Fifth St., Des Moines, Iowa.  
Findley, Park A., 617 Walnut St., Des Moines, Iowa.  
Fulton, Robert R., 413 Bellefontain, Kansas City, Mo.  
Harpster, W. C., 1151 Wightman St., Pittsburgh, Pa.  
Harris, Robt. W., c/o British American Chem. Co., Ltd., 371 Aqueduct St., Montreal, P. Q., Canada.  
Hartmann, Bernhard G., 4404 Magnolia Ave., Chicago, Ill.  
Hicks, Russell E., Yale & Towne Mfg. Co., Stamford, Conn.  
Hitchens, A. Parker, Glenolden, Pa.  
Hodges, Frank, College Station, Texas.  
Hoseason, James H., 2 Bridge St., Manchester, England.  
Keefer, Norman D., Chambersburg, Pa.  
Larson, Victor, South Bend, Wash.  
Levin, Isidore, 5739 Calumet Ave., Chicago, Ill.  
Logan, John Fremont, 5815 Drexel Ave., Chicago, Ill.  
Loomis, C. C., 316 Woodworth Ave., Hastings-on-Hudson, N. Y.  
Macaulay, J. R., 2378 Hutchison St., Montreal, Canada.  
Masten, P. W., 507 Union Oil Bldg., Los Angeles, Calif.  
Nicholas, Chas. B., 1786 Main St., Northampton, Pa.  
Petrie, J. W., 325 Newton-Claypool Bldg., Indianapolis, Ind.  
Ransom, George F., 2600 Eighteenth Court, Ensley, Ala.  
Rising, Walter H., 165 Bridge St., Corning, N. Y.  
Sauer, Verra L., 3401 Wells St., Milwaukee, Wisc.  
Schultz, G. W., 57th & Butler Sts., Pittsburgh, Pa.  
Showalter, H. C., Wabash, Ind.  
Sipler, H. T., 102 Ninth St., Darby, Pa.  
Snow, W. C., 1229 Third Ave., Salt Lake City, Utah.

Stockelbach, F. E., Terminal Factory, Hoboken, N. J.

Sullivan, Theodore G., Jr., Box 17, Stelton, N. J.

Thompson, Thos. G., 5212 Eighteenth Ave., N. E., Seattle, Wash.

Wicks, Alfred, 1404 Alberni St., Vancouver, B. C., Canada.

Woods, George James, 2 Branksome Rd., Merton, London, S. W., England.

Wright, T. Archibald, Box 4, New Market, N. J.

Young, Alexander B., 1001 Livingston Hall, Columbia University, New York City.

[Full accounts of all meetings should be sent to Secretary Charles L. Parsons, Box 505, Washington, D. C.]

## MEETINGS OF THE SECTIONS.

### WESTERN NEW YORK SECTION.

The annual meeting was held May 27. The following officers were elected for the ensuing year: *President*, J. G. Melendy; *1st Vice-President*, Dr. J. A. Miller; *2nd Vice-President*, Dr. Albert Sy; *Secretary*, David H. Childs; *Treasurer*, Leslie E. Chamberlain; *Ex. Comm.*, Ray W. Lindsay, Dr. W. H. Stanton, R. H. White. *Councilors*, W. J. Watkins, Walter Wallace.

R. H. WHITE, *Secretary*.

### PUGET SOUND SECTION.

The regular meeting was held June 22. Dr. Horace G. Deming, head of the department of chemistry in the University of the Philippines, gave an illustrated lecture on "The Resources and Industries of the Philippines."

H. L. TRUMBULL, *Secretary*.

# Proceedings.

## COUNCIL.

President Herty appointed L. H. Baekeland to represent the Society on the Committee on General Lines of Coöperation between the National Academy of Sciences and Four Engineering Societies.

MEMBERS ELECTED BETWEEN JULY 15 AND AUGUST 15, 1916.

Blanchetiere, Alexandre, Bur. Hygiene, Boulogne-sur-mer, France.  
Borgstrom, Parry, Y. M. C. A., Berkeley, Calif.  
Brunkow, H. E., San Diego Cons. Gas & Elec. Co., San Diego, Calif.  
Campbell, Chas. L., 75 Pitts St., Boston, Mass.  
Cleary, David F., 319 Traphagen St., West Hoboken, N. J.  
Coombs, Richard H., Forest Grove, Waltham, Mass.  
Currier, Richard J., Box 178, Fulton, N. Y.  
Dorrance, Roy L., Chem. Div., Experimental Farm, Ottawa, Canada.  
Fischer, Alfred, Box 1597, Milwaukee, Wisc.  
Francis, Parker, Oxygen Gas Co., Kansas City, Mo.  
Freeman, H. A., Central Expt. Farm, Ottawa, Canada.  
Friedman, Elisha M., 14 Wall St., New York City.  
Hanzelin, Frank C., 24535 Central Park Ave., Chicago, Ill.  
Hoover, Walter, 114 N. Riley Ave., Indianapolis, Ind.  
Horney, Odus C., 120 Broadway, New York City.  
Howe, Charles S., Rose and Calif. Sts., Pasadena, Calif.  
Inouye, Teikichi, 124 Audobon Ave., New York City.  
Jeffries, William J., Jr., 430 S. 55th St., Philadelphia, Pa.  
Jewett, Frederick W., 14 Morningside Ave., New York City.  
Just, Ernest A., 1420 Linden Ave., Long Beach, Calif.  
Lentz, H. L., Box 226, Halstead, Kans.  
Lewis, Edward J., 1655 S. Troy St., Chicago, Ill.  
Lichtenwalter, H. O., Union Powder Corp., Parlin, N. J.  
MacLay, Edgar G., 408 Fifth Ave., N., Great Falls, Mont.  
Massey, J. R., Glass Founders Corp., Milltown, N. J.  
Miller, Geo. E., Cooper College, Sterling, Kans.  
Montgomery, Robert J., H. Koppers Co., Mellon Institute, Pittsburgh, Pa.  
Morgan, Ralph W., 310 N. Illinois St., Indianapolis, Ind.  
Moskowitz, Meyer, 204 Henry St., New York City.  
Nellis, Edward G., 42 West 39th St., New York City.  
Novish, Frank R., 1165 Dorr St., Toledo, O.  
Oberfell, G. G., Homer, O.  
Rutishauser, R., Aetna Chemical Co., 120 Broadway, New York City.  
Sweetland, L. Earl, Penn. Salt Mfg. Co., Wyandotte, Mich.  
Toabe, Kebe, Merrimac Chemical Co., North Woburn, Mass.  
Utsunomiya, M., Aetna Chem. Co. of Canada, Drummondville, Que., Canada.  
VanStone, Nathan E., 3330 Harold Ave., Berwyn, Ill.  
Weiller, Paul, New Brunswick, N. J.  
Woldenberg, 54 West Kinzie St., Chicago, Ill.

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**DECEASED.**

Henry Bowen, Contact Process Co., Buffalo, N. Y., July 15, 1916.

W. S. Gillies, 6443 Kenwood Ave., Chicago, Ill., August, 1916.

Arthur G. Levy, 1923 Madison Ave., New York City, July 12, 1916.

Sir William Ramsay, Hazelmere, Bucks, England, July 23, 1916.

William Simon, Catonville, Md. (charter member), July 19, 1916,

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# Proceedings.

## COUNCIL.

The following have been appointed by President Herty as a Committee on Government Specification of Food and Toilet Articles: L. M. Tolman, Chairman, H. E. Barnard, E. H. S. Bailey.

### MEMBERS ELECTED BETWEEN AUGUST 15 AND SEPTEMBER 15, 1916.

- Bader, Joseph P., 921 Tiffany St., New York City.  
Bangs, Bradley W., Carteret, N. J.  
Bergen, R. C., 239 W. 39th St., New York City.  
Bergquist, J. G., Glen Head, N. Y.  
Blachly, Fred E., care U. S. Zinc Co., Sand Springs, Okla.  
Bovard, William M., Taylor Logan Co., Papermakers, Holyoke, Mass.  
Boyd, R. N., 1826 Turner St., Allentown, Pa.  
Bradshaw, George B., Hotel Davenport, Stamford, Conn.  
Brandel, Irvin W., 3317 Ivison Ave., Berwyn, Ill.  
Breedis, John, 1546 N. Hoyne Ave., Chicago, Ill.  
Bunker, George C., Box 216, Gatun, Canal Zone.  
Butler, E. P., Canadian Explosives, Ltd., Beloeil, Quebec, Canada.  
Campbell, Donald, 195 Montclair Ave., Newark, N. J.  
Clarke, J. O., 130 State Capitol, Atlanta, Ga.  
Conover, Charles B., Rural No. 2, New Brunswick, N. J.  
Cunningham, Noel, 90 West St., New York City.  
Draves, Carl Z., 515 North 42nd St., Seattle, Wash.  
Duffy, J. Houston, 214 E. State St., Olean, N. Y.  
Faust, Thomas A., St. George St., London, Ont., Canada.  
Fonyo, Aladar, 3440 Halliday Ave., St. Louis, Mo.  
Friedemann, Theodore E., East Lansing, Mich.  
Gardner, Harold B., University Club, Altoona, Pa.  
Groten, Frank, Jr., Passaic Metal Ware Co., Passaic, N. J.  
Hummell, August, care Hummell & Roginson, 68 Maiden Lane, New York City.  
Ingalls, Frank P., 1329 Fiftieth St., Brooklyn, N. Y.  
Jolivet, Simeon L., Mt. St. Josephs College, Sta. D., Baltimore, Md.  
Jonson, L. B., West Raleigh, N. C.  
Kellogg, C. M., 1012 Twelfth St., Douglas, Ariz.  
Lang, Felix, care Union Powder Corporation, Parlin, N. J.  
Latimer, Wendell M., 1700 Tenn. St., Lawrence, Kans.  
Lazrus, Samuel M., Standard Aniline Products, Inc., Newburgh, N. Y.  
Levey, Harold A., 3801 Grand Blvd., Chicago, Ill.  
Maenpaa, John W., 21 Chapel St., Norwood, Mass.  
Mantius, Otto, 233 Broadway, New York City.  
Maxwell, Arthur B., Sante Fe Gold & Copper Mining Co., San Pedro, N. Mex.  
McKeefe, Edward P., 50 East 41st St., New York City.  
Mitchell, Harold S., 6126 Ellis Ave., Chicago, Ill.  
Pervier, Norville C., 211 So. Hyland, Ames, Iowa.  
Pike, Neal C., 301 West 8th St., Erie, Pa.

Prindle, Edwin J., 111 Broadway, New York City.  
 Proelss, O., United Zinc Smelt'g Corp., Moundsville, W. Va.  
 Radcliffe, David D., Hotel Madison, Perth Amboy, N. J.  
 Richardson, Wilbur P., Cornell, Wisc.  
 Sherwood, Reginald C., State College, Brookings, S. D.  
 Sokal, Evelyn M., 66 West 9th St., New York City.  
 Spencer, Marshall G., 1804 Washington St., Wilmington, Del.  
 Standerline, Bert A., 527 Yale Ave., Youngstown, Ohio.  
 Steinberg, Wm. H., care Hemming Mfg. Co., Garfield, N. J.  
 Stewart, Robert P., 402 Lakeview Ave., Jamestown, N. Y.  
 Stone, Richard H., 170 Buffalo Ave., Niagara Falls, N. Y.  
 Toll, John D., 1010 Arch St., Philadelphia, Pa.  
 Tydeman, F. W. L., care Shell Co. of Calif., Martinez, Calif.  
 Umbreit, Stanton, 912 Shepard Ave., Milwaukee, Wisc.  
 Weiser, Harry B., The Rice Institute, Houston, Texas.  
 Wetmore, Chester, 415 Buchanan St., San Francisco, Calif.  
 Williams, George A., 1093 Central Ave., Dunkirk, N. Y.  
 Wunder, George G., Y. M. C. A., Rock Island, Ill.

### MEETINGS OF THE SECTIONS.

[Full accounts of all meetings should be sent to Secretary Charles L. Parsons, Box 505, Washington, D. C.]

#### CHICAGO SECTION.

The regular meeting was held September 15. Program: "The Manufacture of Synthetic Phenol," by Prof. Harry McCormack; "Synthetic Phenol Resins for Printing Plates—A Special Application of Anhydrous Resins," by L. V. Redman, A. J. Weith and F. P. Brock.

D. K. FRANCE, *Secretary*.

#### ROCHESTER SECTION.

The following officers were elected and served during the term 1915-16, but inadvertently they have not been published heretofore: *Chairman*, Harry A. Carpenter; *Vice-Chairman*, Chas. F. Hutchison; *Secretary*, H. H. Tozier; *Treasurer*, J. E. Woodland; *Councilor*, H. E. Howe.

H. H. TOZIER, *Secretary*.

#### DECEASED.

Charles S. Champion, Savona, N. Y. Died July 31, 1916.

Francis Wyatt, 402 W. 23rd St., New York City. Died September, 1916.

Charles C. Steere, 3320 Reading Road, Cincinnati, Ohio. Died September, 1916.

# Proceedings.

## GENERAL MEETING.

The 53rd meeting of the American Chemical Society was held in New York City from Monday, September 25, to Saturday, September 30, 1916. The meeting opened with a Council meeting at 4.00 P.M. at The Chemists' Club, with sixty-eight Councilors present, dinner being served to the Council two hours later as guests of the New York Section.

On Tuesday morning, September 26, at Columbia University, the meeting was opened by Chairman J. Merritt Matthews, of the New York Section of the Society, followed by addresses of welcome from Health Commissioner Dr Haden Emerson, of the City of New York, and President Butler, of Columbia University. Charles H. Herty, President of the American Chemical Society, made a fitting response. There was then presented a communication from Dr. J. McKeen Cattell, Chairman of the Committee on Policy of the American Association for the Advancement of Science, requesting the American Chemical Society to hold an adjourned meeting in New York City with Section C of the American Association for the Advancement of Science during Convocation Week, 1916-1917, this being the intent of the vote passed by the Council of the American Chemical Society at Cincinnati. It was unanimously voted by the chemists assembled that this meeting be adjourned to Convocation Week, 1916-1917, for the purpose of participating in the sessions of Section C of the American Association for the Advancement of Science to be held in New York City during that week. It was voted that the Secretary be instructed to give notice of this adjourned meeting to all members of the Society not later than November 1, and that it also be announced in the *Journal of Industrial and Engineering Chemistry* for December. Two papers were then read in general meeting as follows: Wilder D. Bancroft, "Outline of Colloid Chemistry;" Horace C. Porter, "Coal and Coke By-Products as a Source of Fixed Nitrogen" (illustrated).

On Tuesday afternoon a public meeting was held in the Horace Mann Auditorium of Columbia University with papers as follows: "Chemistry and the National Welfare," Gen. William Crozier, Chief of Ordnance, War Department; "Chemistry and Banking," John E. Gardin, Vice-President National City Bank; "Expanding Relations of Chemistry in America," Charles H. Herty, President American Chemical Society.

At 8.00 P.M., a reception to the visiting members of the Society, guests, members of the American Electrochemical Society and members of the Technical Association of the Pulp and Paper Industry was given by the New York Section at Hotel Astor. Refreshments were served, and dancing was in order during the latter part of the evening.

Meetings of Divisions were held on Wednesday, Thursday, Friday and Saturday mornings, and two special industrial conferences were held on Wednesday, Thursday, and Friday afternoons and Saturday morning. These industrial conferences were a feature of the meeting and were largely attended. The subjects of the conferences were as follows: "American Dye-Stuff Manufacture," Chas. H. Herty, Presiding; "Electric Furnace Steels and Alloy Steels," John A. Mathews, Presiding; "American-Made Chemical Glass and Porcelain," Arthur H. Thomas, Presiding; "Industrial Alcohol, Acetone, and Acetic Acid," Arthur D. Little, Presiding; "Manufacture of Paper Pulp and By-Products," Robert B. Wolf, Presiding; "Medicinal Chemicals," Harold Hibbert, Presiding; "Miscellaneous Chemical Industries: Convertibility of Plant," William H. Grosvenor, Presiding; "Oils and Motor Fuels," Raymond F. Bacon, Presiding.

A very successful symposium on colloids, both theoretical and applied, was a feature of the general session of the Biochemical, Physical and Inorganic, and Industrial Divisions. On Friday morning the Division of Industrial Chemists and Chemical Engineers held a symposium on occupational diseases in chemical trades.

The Rubber Section again met, after some two years' inactivity, with over one hundred members present, and held a very successful meeting.

On Friday evening, members and guests sat down to a banquet at the Waldorf Astoria with over four hundred present. The banquet was one which will be long and pleasantly remembered by those present.

The Second National Exposition of Chemical Industries afforded members a wonderful opportunity to come in touch with the advance which has taken place in chemical industries during the last two or three years and to familiarize themselves with the materials available for the chemists' use in both the laboratory and plant.

The meeting was the largest ever held by the American Chemical Society where registration was taken, nineteen hundred and five members and guests registering for the meeting. The meeting was a success in every particular, and great credit is due to the management of the local New York Section for the way the details were handled and the care with which the comfort of every member attending the meeting was considered.

Full details of the meeting with titles of papers read will be found in the October issue of the *Journal of Industrial and Engineering Chemistry*. The minutes of the Divisions will be found on the pages following.

CHAS. L. PARSONS, *Secretary*.

#### **DIVISION OF AGRICULTURAL AND FOOD CHEMISTRY.**

The meeting was called to order at 9.30 A.M., September 26, by

T. J. Bryan, who was acting chairman on account of the absence of Chairman Tolman.

The following officers were elected for the ensuing year: *Chairman*, T. J. Bryan; *Vice-Chairman*, L. P. Brown; *Secretary*, G. F. Mason. Executive Committee: L. M. Tolman, W. D. Bigelow, A. V. H. Mory.

The meeting adjourned at 12.30 noon.

G. F. MASON, *Secretary*.

#### DIVISION OF BIOLOGICAL CHEMISTRY.

The joint meetings of the Divisions of Biological Chemistry, Physical and Inorganic Chemistry, and Industrial Chemists and Chemical Engineers were attended by a large audience and much interest was evident. The following sessions on Friday and Saturday were devoted to the general program of the Division and were again attended by an interested and enthusiastic audience. At the annual meeting held at the close of the sessions, the following officers were elected for the ensuing year: *Chairman*, C. L. Alsberg; *Vice-Chairman* and *Secretary*, I. K. Phelps. Executive Committee: W. D. Bancroft, *Chairman*, E. Kremers, A. W. Dox, W. R. Bloor, R. E. Swain.

It was also voted that the Executive Committee be requested to consider the advisability of amending the By-Laws to make the annual meeting of the Division the special order of business at the opening of the second session of the September meeting rather than at the close of the sessions.

ISAAC KING PHELPS, *Secretary*.

#### FERTILIZER DIVISION.

The meeting, held in Rumford Hall, The Chemists' Club, was called to order Wednesday morning, September 27, by Chairman Breckenridge, in accordance with the official program.

On motion, the minutes of the previous meeting were dispensed with.

Reports of the following committees were read and accepted: Committee on Fertilizer Legislation, *Chairman*, F. B. Carpenter; Committee on Research and Methods of Analysis, *Chairman*, Paul Rudnick.

On motion, the following Special Committee on Methods of Analysis was appointed by the Chairman: F. S. Lodge, *Chairman*, W. J. Jones, C. H. Jones, F. B. Carpenter, S. W. Wiley.

The following officers were elected: *Chairman*, J. E. Breckenridge; *Vice-Chairman*, L. L. Van Slyke; *Secretary*, F. B. Carpenter. Executive Committee: Paul Rudnick, R. N. Brackett, C. H. Jones, H. J. Wheeler.

No other business appearing, the meeting was adjourned.

F. B. CARPENTER, *Secretary*.

### DIVISION OF INDUSTRIAL CHEMISTS AND CHEMICAL ENGINEERS.

The Division of Industrial Chemists and Chemical Engineers met in Schermerhorn Hall, Columbia University, September 25, 26 and 27, 1916, with H. E. Howe as Chairman and S. H. Salisbury, Jr., Secretary. The Secretary had no report.

The Division voted to amend Article IV of the By-Laws so that it shall consist of the first sentence only.

The Committee on the Analysis of Fats and Oils, through its Chairman, W. D. Richardson, handed in a report upon its work since the Urbana meeting.

The Thursday meeting was taken up with a symposium on Colloids in conjunction with the Division of Biological Chemistry and the Division of Physical and Inorganic Chemistry.

The Friday meeting consisted of a symposium on Occupational Diseases in the Chemical Trades.

The nominating Committee reported the following names for officers, who were duly elected: *Chairman*, H. E. Howe; *Vice-Chairman*, R. F. Bacon; *Secretary*, S. H. Salisbury, Jr. Executive Committee: W. F. Hillebrand, C. H. Herty, H. K. Benson, J. R. Withrow, S. W. Parr. S. H. SALISBURY, JR., *Secretary*.

### DIVISION OF ORGANIC CHEMISTRY.

The Organic Division held its meeting in the gymnasium at Columbia University during the mornings of September 27 and 28. A committee, consisting of Messrs. Frankforter, Hudson, and Nicolet, was re-appointed to make arrangements for a joint meeting with the Division of Physical and Inorganic Chemistry at the next general session.

The following officers were elected for the coming year: *Chairman*, J. R. Bailey; *Vice-Chairman* and *Secretary*, H. L. Fisher. Executive Committee: F. B. Allan, C. G. Derick, E. E. Reid.

H. L. FISHER, *Secretary*.

### DIVISION OF PHARMACEUTICAL CHEMISTRY.

Chairman Long was present and presided. L. F. Kebler was appointed to act as secretary in the absence of Secretary Beal.

The following officers were elected for the ensuing year: *Chairman*, L. F. Kebler; *Secretary*, Geo. D. Beal.

L. F. KEBLER, *Acting Secretary*.

### DIVISION OF PHYSICAL AND INORGANIC CHEMISTRY.

Meetings were held on Wednesday, September 27, and Thursday, September 28, in conjunction with the Division of Biological Chemistry and the Division of Industrial Chemists and Chemical Engineers, the subject under general discussion being Pure and Applied Colloid Chemistry. On Friday, September 29, after the conclusion of the Colloid

Symposium, the Division proceeded to its own program and the election of officers.

The following nominees for officers of the Division for the year 1916-1917 were unanimously elected: *Chairman*, T. W. Richards; *Vice-Chairman*, H. P. Cady; *Secretary*, Earl B. Millard. Executive Committee: A. W. Browne, F. K. Cameron, W. E. Henderson, A. B. Lamb, I. Langmuir.

JAMES KENDALL, *Secretary*.

#### DIVISION OF WATER, SEWAGE, AND SANITATION.

The minutes of the last previous meeting were read and approved.

The following officers were elected for the ensuing year: *Chairman*, R. B. Dole; *Vice-Chairman*, E. H. S. Bailey; *Secretary*, H. P. Corson. Executive Committee: The above officers, *ex officio*, E. B. Phelps, Edward Bartow.

The meeting then adjourned.

H. P. CORSON, *Secretary*.

#### RUBBER SECTION.

The Rubber Section met on Thursday morning in Rumford Hall, The Chemists' Club, with L. E. Weber in the chair and J. B. Tuttle, secretary. About seventy-five persons were present at the opening, which increased to one hundred later. An active discussion followed on "The Accelerated Life Test of Rubber Compounds." The papers presented will be found in the October issue of the *Journal of Industrial and Engineering Chemistry*. It was voted to leave the arrangements for further meetings with the chairman and secretary, who are to consult with the proper officers of the Society in this regard. A stenographer was present, who took down a large portion of the discussion on the topic above-mentioned, which, in revised form, will be printed for the benefit of the rubber industry in the *India Rubber World*.

J. B. TUTTLE, *Secretary*.

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#### DIRECTORS' MEETING MINUTES.

The Directors met at The Chemists' Club at 9.30 A.M., September 27, 1916. Messrs. Herty, Bogert, Bigelow, Little, Love, Smith and Parsons were present.

It was voted that the secretary be directed to accept subscriptions to the journals on a basis of full volumes only.

It was voted that the secretary be authorized to turn over to the Eschenbach Printing Company the waste paper from excess journals recently taken from stock in consideration of their reprinting, without other recompensation, THIS JOURNAL, Volume 29, Number 5.

It was voted to appropriate the sum of \$50.00 for the expenses of the Chairman of the Priestley Memorial Committee, covering clerical, stationery, and similar expenses.

It was voted that \$150.00 be added to the Secretary's clerical account budget and \$250.00 to his budget for general expenses.

It was voted that necessary expenses under incidental account be appropriated and the amount be paid from general funds or transferred from other appropriations not otherwise used.

It was voted that the communication of the Advertising Committee regarding the *Industrial Journal* be adopted in principle and that the Directors unanimously recommend to the Council the election of Charles H. Herty as Editor.

In view of the fact that the Directors are the responsible trustees of the Society it was voted to recommend that the power of the Council be and hereby is delegated to the Directors to elect the Treasurer of the Society.

It was voted that in the opinion of the Directors it is very desirable that the American Chemical Society undertake as soon as possible the publication of a journal of popular chemistry along lines similar to those outlined in the report of Director A. D. Little upon this subject. With this in view it was recommended that the Council request the President to appoint a Committee of three, of whom A. D. Little shall be Chairman and C. H. Herty one of the members, to secure a guarantee fund of not less than \$50,000; to recommend an editor and a business manager to be employed by the Directors; and to take such other preliminary steps as in their judgment it deems wise.

An adjourned meeting of the Directors was held at The Chemists' Club, Thursday, September 27, at 10.30 A.M. Directors Herty, Love, Smith, Bigelow, Bogert and Parsons were present.

Mr. E. J. Crane appeared before the Directors with certain inquiries regarding the issuance of the Decennial Index to *Chemical Abstracts*.

It was voted that the Index to *Chemical Abstracts* should contain no advertisements.

Besides the regular paper binding offer of the Decennial Index to *Chemical Abstracts*, it was voted to offer one form of binding and one form only at a price sufficient to cover all costs involved, the binding to be a dark brown buckram.

It was voted that payment for the Index to *Chemical Abstracts* be asked for when the first volume is ready for delivery.

It was voted that Charles H. Herty be added to the Advertising Committee, and that the Committee be asked to formulate a plan for the future conduct of the advertising office, and, after obtaining the consent of the Directors, that they be authorized to put it into force.

It was voted that the Editor of the *Journal of Industrial and Engineering Chemistry* shall receive a salary of \$6,000 per annum, beginning with the fiscal year December 1st next.



By authorization of the Council, the Directors elected E. G. Love Treasurer of the Society with the purpose of consolidating the offices of the Treasurer and the Chairman of the Finance Committee.

The Directors passed a vote of thanks to A. P. Hallock and directed the Secretary to express to him their appreciation of his long service as Treasurer of the Society.

The directors voted that the salary of A. P. Hallock be continued in the form of an honorarium for the fiscal year beginning December 1, 1916.

### COUNCIL.

President Herty has appointed M. T. Bogert, W. R. Whitney and C. L. Alsberg, to represent the Society on the General Committee of Chemical Research of the National Research Council and the American Chemical Society.

President Herty has appointed Dr. Eugene F. Smith as a member of the Priestley Memorial Committee.

### Council Minutes, New York Meeting.

The Council of the American Chemical Society met on Monday, September 25, at 4.00 P.M., in Rumford Hall, 'The Chemists' Club, New York City, with the following Councilors present: F. C. Atkinson, L. H. Baekeland, J. T. Baker, G. F. Barton, Edward Bartow, Chas. Baskerville, H. D. Batchelor (sub.), W. D. Bigelow, M. T. Bogert, R. N. Brackett (sub.), W. P. Bradley, J. E. Breckenridge, T. J. Bryan, S. R. Church, C. E. Coates, W. F. Coover, E. J. Crane, A. L. Day, C. G. Derick, A. C. Fieldner, G. B. Frankforter, J. S. Goldbaum, W. J. Hale, B. C. Hesse, E. F. Hicks, J. I. D. Hinds, H. E. Howe, C. S. Hudson, W. L. Jennings, E. S. Johnson (sub.), T. B. Johnson, John Johnston, C. M. Joyce, A. C. Langmuir, Irving Langmuir, A. D. Little, J. H. Long, E. G. Love, A. Lowenstein, W. J. McCaughey (sub.), H. McCormack, H. N. McCoy (sub.), D. F. McFarland (sub.), R. H. McKee, K. G. MacKenzie, E. W. Magruder, J. M. Matthews, A. V. H. Mory (sub.), W. A. Noyes, T. J. Parker, S. W. Parr, I. K. Phelps (sub.), F. C. Phillips, Ira Remsen, W. K. Robbins, W. P. Schuck (sub.), Alexander Smith, Julius Stieglitz, W. T. Taggart, A. N. Taylor, J. E. Teeple, F. E. Tuttle, W. H. Watkins, R. C. Wells, David Wesson, A. S. Wheeler, M. C. Whitaker, W. A. Whitaker (sub.), H. W. Wiley, J. L. Wills (sub.).

A communication from the Conference Committee on National Preparedness, asking the support of the American Chemical Society for national preparedness, was read. The communication was referred to the President, Secretary, and Charles Baskerville, for report.

A communication was received from the New York Section of the American Chemical Society, requesting the President of the Society to appoint

a central committee from representatives of the universities and the industries to study opportunities and to make recommendations for co-operation along the lines laid down in the conclusions arrived at as a result of the activities of the committee of the New York Section. (See page 658, July, 1916, issue *Journal of Industrial and Engineering Chemistry*.) The President was authorized to appoint such committee, the number to be left to his discretion, and to be added to at will.

A communication was presented from the Chairman of the National Vigilance Committee of the Associated Advertising Clubs, asking the assistance of the American Chemical Society in passing upon questionable advertisements relating to chemical subjects. It was voted to refer the communication to the Committee on Government Specifications of Food and Toilet Articles.

A communication was received from the Committee on Publicity regarding the desirability of the proper dissemination of chemical information to the public, which was referred to the Directors with the approval of the Council for such action as they deem wise.

Invitations from the Cleveland Section and from the Northeastern Section to hold the next annual meeting of the Society in Cleveland and Boston, were read. After careful consideration of the subject, it was voted that the invitation of the Northeastern Section be given preference over the Cleveland Section, for geographical reasons, as the Spring meeting is to be held in Kansas City.

It was voted that the next annual meeting be held between September 1 and September 10, 1917, in Boston, Mass. The Secretary was instructed to express the thanks and appreciation of the Council to the Cleveland Section for their kind invitation to meet with them next year.

The Committee on Professional Ethics submitted the following report:

### **Majority Report of the Committee on Professional Ethics.**

#### **I.**

The first obligation upon the chemist is a scrupulous regard for truth.

#### **II.**

Chemistry has become a science through the coöperative effort of tens of thousands of earnest seekers after truth. The chemists should recognize their obligation to these workers and to the community which has provided opportunities for study and research. They should give due credit to the one and loyal service to the other.

#### **III.**

As good citizens it is the duty of chemists to be ever vigilant for the welfare of the community and to bear their part in sustaining its institutions and its burdens. They should welcome and make use of op-

portunities to educate the public to a true appreciation of the dignity and usefulness of their profession.

## IV.

Chemists should endeavor to inculcate sound ideas in the public mind regarding chemical facts and theories, and from the nature of their work and training should be uncompromising enemies of fraud in every form. In its suppression they should not be content with passive resistance and a merely personal honesty but should take an active and aggressive part.

## V.

In their relations to each other chemists should strive to promote mutual helpfulness, mutual understanding, mutual encouragement in scientific work and in all good endeavor. They should cultivate mutual forbearance, fraternal courtesy and a broad and generous fellowship.

## VI.

In their relations to their employers chemists should constantly remember that they are practising a profession of honor and dignity which places service before gain. They should undertake no work for which they are not qualified by training, but should refer their client to a properly qualified specialist in such work.

## VII.

Self respect and a due regard for their obligations to each other require chemists to make proper charges for work done, information furnished or opinions rendered in the course of business or professional practice. In the estimation of such charges consideration should be given to the various factors entering into the cost and value of the service, as the responsibility involved, the time and equipment required, the general custom of the profession in the locality concerned and the special value of the service.

## VIII.

The chemist stands in a fiduciary relation to his employer and should in no case accept financial or other compensation from more than one party in interest without the knowledge and consent of all parties. He should not disclose to others the contents of certificates or reports to clients without the written consent of the client concerned. The chemist should treat as confidential all communications of his client, and should guard, more carefully than his own, his client's interests in all matters entrusted to him.

## IX.

The chemist should not accept conflicting retainers or represent conflicting interests or identify himself with other than legitimate and well considered enterprises. He should endeavor to protect all reputable chemists from misrepresentation.

## X.

The client is entitled to painstaking and accurate work by recognized and accepted methods, and to the best information and advice which it is within the power of the chemist to give. Reports should be dignified in form and substance, careful and conservative in statement, and as definite in their conclusions as the facts permit.

Clients should recognize that inconsistencies in results sometimes secured by different chemists are often due to actual differences in the samples submitted by the client and are thus in fact an evidence of careful work. They should be slow to attribute these inconsistencies to incompetency or unworthy motives.

## XI.

It is desirable for the public welfare and prosperity that chemical investigations be conducted without undue restriction in institutions which maintain courses for the education and training of chemists and that the instructing staff in such institutions be permitted to turn their special knowledge and experience to the direct service of individual clients and to charge therefor a proper compensation, but it is prejudicial to the best interests of chemistry for such service to be rendered in unfair competition with the profession at large at charges which ignore the usual costs of equipment and conduct of the work.

## XII.

The obligations of the chemist and the community are reciprocal. To the community the chemist owes his training and his opportunity for service, and in this service he should expend his best endeavor. To chemists the community owes in far larger measure than it yet appreciates, its comfort, protection, prosperity and breadth of intellectual view. The well-being of the community requires due provision for the teaching of chemistry and the promotion of research and such encouragement of the study and practice of chemistry as may be derived from adequate compensation and the recognition which is based on understanding.

Respectfully submitted,

(Signed) ARTHUR D. LITTLE, *Chairman*,  
L. H. BAEKELAND,  
WILLIAM BRADY,  
F. K. CAMERON.

**Minority Report.**

The chemists of this country may be classified roughly as consulting chemists, works chemists, government chemists, and teaching chemists, though any one man may belong in several groups or even in all at once. The interests of the groups diverge so much that it seems impossible to devise a single code unless we limit it to platitudes.

While the American Chemical Society does not in any way encourage the betrayal of professional secrets, it has always stood hitherto for the freest discussion possible under existing circumstances. It would be a distinct step backwards to adopt officially a rule that no chemist should discuss professional matters unless he has received written permission from his employer. In a great many cases this rule or something similar is enforced by employers; but the American Chemical Society should encourage and not discourage the belief that a chemist is a person of discretion. The rule, as worded, would require a college chemist to obtain written permission of the president or trustees before publishing any paper. This will not be done and it is not the intention of the committee that it should be done; but a code that requires interpretation and that is not to be lived up to, is worse than no code at all because it makes us a laughing-stock.

The proposed code was written by a consulting chemist for consulting chemists. It is an admirable one for that purpose; but it should not be adopted by the American Chemical Society as a general code applicable to all members.

WILDER D. BANCROFT.

After discussion, the Minority Report, which referred to Section VIII of the Majority Report, was voted down, it being considered by the majority of the members that the word "client" in Section VIII of the Majority Report, to which it referred, was distinctive.

After discussion of the Majority Report, it was voted to refer this Report to the local sections of the Society for discussion, and that it be taken up again at the annual meeting of the Society in September, 1917.

The Council then adjourned for dinner, and re-assembled at 8.30 P.M., when the Report of the Committee on Business Management, presented first to the Council at the Cincinnati meeting and made a special order for this meeting, was taken up.

After several hours' discussion, it was voted to lay both the Majority and the Minority Report of the Committee on Business Management on the table, and to discharge the Committee.

The following communication, prepared at the request of the Advertising Committee, who had for some weeks been considering the question of the business arrangements of the *Industrial Journal*, was read to the Council, the Council also being informed at the same time that Dr. Whitaker could under no condition continue as Editor of the *Industrial Journal* on account of pressure of other duties.

### **The Future of the Industrial Journal.**

Six years of daily contact with the numerous problems of building up and developing the *Journal of Industrial and Engineering Chemistry* would naturally bring out some observations which I have been urged to place, briefly, before the Directors for their consideration and discussion.

The *Industrial Journal*, as the organ of the American Chemical Society, should occupy a commanding position among technical publications of this country, instead of being as it is now, simply a medium for the publication of original papers of and for members of the Society, with the added opportunity for impressing personal views and opinions of members upon each other.

The Journal should be in a position to cement and unify the interests of the chemical profession, to develop and improve the ethical standards of chemists, to collect and distribute all knowledge which will make for higher chemical engineering achievements, to draw us to—not to separate us from—other engineering professions, to take and to hold a position squarely representing the profession before the public, and to be a real factor in moulding and directing national policies in which the chemical profession has a right to be heard.

The very fact that the Journal has the backing of a great technical society should give it a position of strength for enhancing its influence and for bestowing substantial benefits on the profession which supports it. Its policy and outlook should be big and broad enough to make its influence felt not only inside the society, but outside; not only on purely chemical matters, but matters of general technical and engineering value; not only in scientific matters, but the relations of the chemical profession to great public or national problems.

The *Industrial Journal* is essentially a product of evolution. It had to begin in a small way, due to lack of resources of the Society and the absence of editorial experience. The management of the publication up to the present has been, as a matter of necessity, amateurish. Heretofore the resources of the Society and the earning power of the publication did not justify the employment of an adequate organization to develop the Journal along its lines of greatest opportunity.

Have we not now reached the turning point? Is this not the time and place to accept an obvious opportunity—almost an obligation—and put the *Industrial Journal* upon a sound permanent footing, and give it the means to do its best?

The *Industrial Journal* is now more than self-supporting. The income from advertising has been increasing steadily as a result of the most strenuous work in overcoming handicaps imposed by our lack of experience and adequate facilities. The present advertising income plus a reasonable allowance from the membership dues of the Society, for subscription price, places to the credit of the Journal operating account a handsome profit which is now commandeered by the Society and used for other purposes. This surplus alone, reinvested in the *Industrial Journal*, would supply ample funds for the reorganization of the publication upon a new and sound basis.

Inadequate funds and lack of experience cannot now, therefore, be urged

as a reason for our failure to take advantage of the opportunity and the obvious need of the publication.

### **The Remedy.**

*First.* Develop comprehensive editorial policies.

The power and influence of any publication is developed through the soundness and consistency of its editorial utterances. The *Industrial Journal* has at present no editorial policy. In the past such articles as have been published as editorials have been of a hit-and-miss character, representing the expression of individual views, summaries of industrial developments, descriptive articles covering Society meetings, and now and then an effusion on some particular hobby of a chemist, by a chemist, for a chemist. It is obvious that such a variety of matter, which flows more or less irregularly, cannot be characterized as an editorial policy. A system of shopping around among the associate editors and various members of the Society for editorial articles could not possibly achieve the needed consistent editorial policy.

A comprehensive editorial policy would result from the selection of a *real editor* who would devote his entire time (1) to the study of the Society's problems, (2) to the consistent editorial development and discussion of its needs, (3) to the editorial treatment of questions of public and national interest in which the Society is concerned, and (4) to the general development of an editorial policy which would make the Journal known both at home and abroad as the authoritative representative of the views, aims, ethics and sphere of influence of the chemical profession in America.

*Second.* Provide adequate and well equipped editorial and business quarters for the Journal.

At the present time the editorial headquarters are squeezed into a bottle storage room (see photographs and plan attached) with a single window, where four or five people struggle with the innumerable editorial duties, under conditions of congestion which would not be permitted in many factories.

Quarters befitting the dignity of the Society and the chemical profession should be provided in New York City for both the editorial headquarters and the advertising department.

*Third.* Editorial assistance, proof-readers and clerical help should be provided in sufficient quantity, and of such quality that the routine work of the office might proceed regularly and methodically, without periods of excessive strain. Furthermore, this arrangement should provide reasonable vacation allowances, without doubling the burdens of co-workers.

*Fourth.* The news gathering facilities of the Journal should be developed at once, by providing staff reporters to cover all technical and engineering society and convention meetings.

*Fifth.* Foreign and domestic engineering and industrial news should be reviewed promptly and regularly, for the benefit of the readers of the Journal. The trend of industrial progress should be forecasted from a close study of foreign and domestic patent literature.

*Sixth.* Competent staff writers should be provided to investigate and report upon important plant, process, and equipment improvements. The Journal should publish each month, at least one good illustrated article by such a staff representative, describing some of the new plants or processes constantly being developed in this country. Such articles should include engineering, power, labor, organization, costs, insurance, industrial hazard, market, competitive and other conditions affecting manufacturing success.

To continue the *Industrial Journal* along its present lines, with a make-shift part-time editor, with no fixed editorial policy or aim, with no headquarters nor adequate staff for its operation and development, with no coördination of its interests and no controlling hand for its future, will in my humble opinion lead to its ultimate failure.

On the other hand, the time is ripe, and the way is now clear, to take the Journal from its present state of development, which has been attained at such cost in labor and effort, and place it upon a foundation from which it can develop into an influence and power both within and outside of the chemical profession.

M. C. WHITAKER,

*Editor, Journal of Industrial and Engineering Chemistry.*

After a short discussion, it was moved and voted that the above communication be referred to the Directors, with the request that they consider it and report their opinion of its advisability to the Council at an adjourned meeting to be held Wednesday evening, September 27.

The Council then adjourned.

An adjourned meeting of the Council was held in Rumford Hall, The Chemists' Club, September 27, at 8.00 P.M., with the following Councilors present: F. C. Atkinson, L. H. Baekeland, W. D. Bancroft, G. E. Barton, Edward Bartow, Charles Baskerville, W. D. Bigelow, F. M. Boyles, R. N. Brackett (sub.), T. J. Bryan, C. E. Coates, E. J. Crane, C. G. Derick, A. C. Fieldner, G. B. Frankforter, A. P. Hallock, B. C. Hesse, E. F. Hicks, W. H. Hollingshead, H. E. Howe, W. L. Jennings, E. S. Johnson (sub.), A. C. Langmuir, A. D. Little, J. H. Long, A. Lowenstein, H. N. McCoy (sub.), R. H. McKee, K. G. MacKenzie, E. W. Magruder, J. M. Matthews, A. V. H. Mory (sub.), W. A. Noyes, T. J. Parker, I. K. Phelps (sub.), F. C. Phillips, W. P. Schuck (sub.), Alexander Smith, F. E. Tuttle, J. E. Teeple, R. C. Wells, David Wesson, A. S. Wheeler, M. C. Whitaker, W. A. Whitaker (sub.), H. W. Wiley, J. L. Wills (sub.).

The following two proposed amendments to the By-Laws suggested



at the Urbana Meeting of the Society, as noted on page 74 of the Proceedings for June, were considered:

1. The Chairman of the Committee on Membership shall submit a monthly report for publication in the Proceedings of the Society which gives the name, residence, and occupation of each nominee, and the names and residence of his nominators. Final action shall be taken by the Committee on these names only after thirty days have elapsed since the publication in the Proceedings.

2. Any motion for the expulsion of any member of the Society shall be submitted first in confidence (without further divulging the name of the member) to the President of the Society with a full statement of the *prima facie* evidence on which the motion is based. The President, in conjunction with the two ex-Presidents preceding him most immediately in office, shall form a Committee with full power to decide whether the motion shall be dropped without further action and without report to the Council; whether the accused member shall be allowed to resign without report to the Council, or whether the motion shall be referred, without prejudice, to a special committee of the Council for further investigation and report to the Council.

The report of the Committee appointed by President Herty to report on this matter is as follows:

"The Committee on the By-Laws proposed at the Urbana meeting, respectfully report that we consider the first By-Law proposed (see p. 74 of the Proceedings for June) unnecessary and undesirable. The second By-Law proposed seems to us suitable and we recommend its adoption.

W. A. NOYES,  
M. T. BOGERT,  
F. K. CAMERON."

The Council voted unanimously to reject the first proposed By-Law, printed above, and to adopt the second, amended to strike out the words "without prejudice," so that the By-Law adopted by the Society reads as follows:

"Any motion for the expulsion of any member of the Society shall be submitted first in confidence (without further divulging the name of the member) to the President of the Society with a full statement of the *prima facie* evidence on which the motion is based. The President, in conjunction with the two ex-Presidents preceding him most immediately in office, shall form a committee with full power to decide whether the motion shall be dropped without further action and without report to the Council; whether the accused member shall be allowed to resign without report to the Council, or whether the motion shall be referred to a special committee of the Council for further investigation and report to the Council."

The Committee appointed at the previous Council meeting to pass resolutions regarding national preparedness, offered the following resolution, which was unanimously adopted:

"Resolved, that the Council of the American Chemical Society declares itself to be in favor of an adequate system of national defense. Such a system involving our Army, Navy, coast defences, natural resources, and industrial development should be so designed as to maintain our liberty and preserve our peaceful pursuit of happiness. The system should also be designed with such reserve power as to maintain our honor and integrity, should the same be menaced by foes within or without. To that end we hold ourselves in readiness to serve Our Country in any capacity, but especially in such ways as our abilities best qualify us.

CHAS. H. HERTY,  
CHAS. L. PARSONS,  
CHAS. BASKERVILLE."

The following recommendation of the Directors was presented to the Council:

"In the opinion of the Directors it is very desirable that the American Chemical Society undertake as soon as possible the publication of a journal of popular chemistry along lines similar to those outlined in the report of Director A. D. Little upon this subject. With this in view it was recommended that the Council request the President to appoint a committee of three, of whom A. D. Little shall be Chairman, and Chas. H. Herty one of the members, to secure a guarantee fund not less than \$50,000; to recommend an editor and a business manager to be employed by the Directors, and to take such other preliminary steps as in their judgment it deems wise."

Mr. A. D. Little presented the plan in detail, and it was unanimously voted that the recommendation be adopted, and that the President be authorized to appoint the third member of the committee.

The Directors reported back to the Council, recommending that the plan outlined by M. C. Whitaker, and presented through the Advertising Committee, be adopted in principle, and that Chas. H. Herty be elected Editor. The Council unanimously adopted this recommendation of the Directors, and Chas. H. Herty was elected Editor of the *Journal of Industrial and Engineering Chemistry* to succeed M. C. Whitaker, resigned.

It was voted that Chas. H. Herty be authorized to recommend his Board of Associate Editors, decreasing the number, if he deemed it advisable, and that the Directors be authorized to elect them.

The Council passed a unanimous vote of thanks, expressing to M. C. Whitaker, Editor of the *Journal of Industrial and Engineering Chemistry*, their sincere appreciation of the splendid and efficient work that he has done as Editor of the *Industrial Journal* during the last six years. The vote was sincere and unanimous.

W. A. Noyes was re-elected Editor of *THIS JOURNAL*, and the following Board of Associate Editors, recommended by him, was also elected: G. P. Baxter, M. T. Bogert, C. A. Browne, Edward Hart, W. F. Hillebrand, John Johnston, J. H. Long, W. Lash Miller, Julius Stieglitz, H. W. Wiley.

E. J. Crane was re-elected Editor of *Chemical Abstracts*.

Chas. L. Parsons was re-elected Secretary.

The following recommendation of the Directors, regarding the Treasurer of the Society, was read:

"Recommended that since the Directors are the responsible trustees of the Society that the power of the Council be and hereby is delegated to the Directors to elect the Treasurer of the Society."

This recommendation was unanimously adopted.

B. C. Hesse made a statement to the Council regarding the work of the "Committee to Cooperate with the United States Government to Obtain the Regular Collation and Publication of Complete and Uniform Statistics in Regard to Foreign Commerce in Chemicals," and asked the help of all local sections to obtain information on imports.

Charles Baskerville called attention of the Council to certain phases of the work on occupational diseases. The whole matter was referred to the Directors of the Society.

Professor Francis C. Phillips made a preliminary report to the Council regarding the Priestley Memorial.

The Council arose and remained standing as a tribute to the memory of Sir William Ramsay and Joseph H. Kastle.

A vote of thanks was passed to the Chairman and members of the New York Section of the Society, and to the chairmen and members of the Committees having in charge arrangements for the New York meeting; to the Chairmen of the Industrial Conferences, to The Chemists' Club, to the officials of Columbia University, to Dean Goetze, Superintendent Norris, and Professor Army, of Columbia University; to Mr. C. I. Fischer, to the management of the Second National Exposition of Chemical Industries, to General Wm. Crozier, to Mr. John E. Gardin, and to those members of the Society and citizens of New York who contributed their automobiles for the entertainment of the ladies, and to the individuals, firms, and corporations who contributed funds and thereby made the meeting a possibility.

The Council then adjourned.

CHARLES L. PARSONS, *Secretary*.

#### MEMBERS ELECTED BETWEEN SEPTEMBER 15 AND OCTOBER 15, 1916.

Allen, A. Holmes, 316 West Grace St., Richmond, Va.

Allen, Henry E., 32 Exchange Place, Providence, R. I.

Allen, Oliver F., Room 1712, 30 Church St., New York City.

Altman, C. A., 1220 Riverview Ave., Kansas City, Kans.

Bailey, Ralph H., 52 Grays Hall, Cambridge, Mass.  
 Bailey, R. J., Du Bois, Pa.  
 Baker, John Shortt, 1409 Jackson St., Wilmington, Del.  
 Beath, O. A., Laramie, Wyo.  
 Beatley, Chas. A., 30 Empedrado, Havana, Cuba.  
 Beers, William H., 2114 First Ave., Birmingham, Ala.  
 Bell, Richard D., 26 Bow St., Somerville, Mass.  
 Blass, Talmadge, Lackawanna Steel Co., Lackawanna, N. Y.  
 Bosworth, H. O., Box 28, Five Corners Station, Jersey City, N. J.  
 Bradley, Charles S., 41 Park Row, New York City.  
 Brennan, J. J., 76 West Third St., St. Paul, Minn.  
 Breth, F. W., 450 High St., Newark, N. J.  
 Britton, Harry C., R. F. D. No. 2, Station A, Syracuse, N. Y.  
 Broadwell, Samuel J., Throop College, Pasadena, Calif.  
 Brophy, Wm. E., 443 Hawthorne Ave., Yonkers, N. Y.  
 Brundage, Edwin W., 27 Beaver St., New York City.  
 Capps, Julian H., Bureau of Mines, Pittsburgh, Pa.  
 Chamberlain, G. E., 443 N. Edward St., Decatur, Ill.  
 Clarke, Hans T., Kodak Park, Rochester, N. Y.  
 Cover, L. E., Armstrong Cork Co., 24th St. & A. V. R. R., Pittsburgh, Pa.  
 Crocker, Ernest C., 505 Washington St., Lynn, Mass.  
 de Stubner, Emile, 1412 State St., Bridgeport, Conn.  
 Dickey, Geo. D., 253 Lafayette Ave., Brooklyn, N. Y.  
 Dougherty, Gerald T., 5406 Harper Ave., Chicago, Ill.  
 Dubin, Minna, 324 Delancy St., Philadelphia, Pa.  
 Dunham, Bertram R., Sinnamahoning, Pa.  
 Ehnts, F. H., 50 Broad St., New York City.  
 Eilberg, Herman, 102 Ritner St., Philadelphia, Pa.  
 Engels, William H., 1 Lincoln Ave., Rahway, N. J.  
 Faber, Henry B., 115 Broadway, New York City.  
 Farquhar, Percival, 49 East 52nd St., New York City.  
 Felder, George, 489 Brooks Ave., West New Brighton, N. Y.  
 Friedmann, Eugen, McLaughlin Chemical Works, Minneapolis, Minn.  
 Fuller, Clarence L., c/o Curtis Bay Distillery, Curtis Bay, Md.  
 Gale, Roger D., Sanford Mills, Reading, Mass.  
 Gephart, Orvon P., Route 1, Miamisburg, Ohio.  
 Gerges, Wesley R., Royersford, Pa.  
 Ginaca, Henry G., 334 Rialto Bldg., San Francisco, Calif.  
 Goldsberry, Albert W., 522 No. New Jersey St., Indianapolis, Ind.  
 Gowdy, Spenser M., 6129 Nassau Road, Philadelphia, Pa.  
 Gray, G. Francis, Wappingers Falls, N. Y.  
 Hamlen, Carleton LeBaron, Butler Chemical Co., Butler, N. J.  
 Hansen, H. W., 51 Danvers St., San Francisco, Calif.  
 Haskell, Geo. O., Southern Cotton Oil Co., Savannah, Ga.  
 Haskell, L. W., Savannah, Ga.  
 Heim, Frederick J., 5 Sophie St., Maspeth, L. I., N. Y.  
 Hendey, Alfred E., 52 Vanderbilt Ave., New York City.  
 Herman, Erle C., c/o Barrett Co., 17 Battery Place, N. Y.  
 Hill, Roland H., Kingston, R. I.  
 Hiron, Gardner, Jr., 300 West 106th St., New York City.  
 Holloway, George T., 13 Emmett St., Limehouse, London, England.  
 Holmes, Andrew A., 1209 Stephen Girard Bldg., Philadelphia, Pa.

- Houston, Jas. W., General Chemical Co., Providence, R. I.  
 Howson, C. E., 37 Liberty Ave., Alliance, O.  
 Hutchinson, John F., Hercules Club, Kenvil, N. J.  
 Isherwood, Percy C. C., Moss Cottage, Bushey Heath, Herts, England.  
 Jackson, Norman L., 313 Meyran Ave., Pittsburgh, Pa.  
 Jacobs, W. M., P. P. G. Co., Charleroi, Pa.  
 Kazmann, Boris, 82 Manchester St., Battle Creek, Mich.  
 Klinkowstern, Jacob J., 77 McKibbin St., Brooklyn, N. Y.  
 Knapp, I. E., Bear Creek Mfg. Co., Petrolia, Pa.  
 Kowalk, Elmer, Palmarito de Canto, Oriente, Cuba.  
 La Mer, Victor K., Cold Spring Harbor, L. I., N. Y.  
 Lange, Alfred R., 200 West 95th St., New York City.  
 Lawford, Harrison B., 1016 Gilpin Ave., Wilmington, Del.  
 Lehman, John K., Highspire, Pa.  
 Lowerfels, Frank H., 1 West 102nd St., New York City.  
 Mains, Gerald H., 609 Y. M. C. A., Washington, D. C.  
 Mann, F. W., Standard Oil Co. of Calif., Richmond, Calif.  
 Martin, R. B., 203 W. 81st St., New York City.  
 McCaffrey, Edward J., 4 President St., Providence, R. I.  
 McDaniel, A. S., Eastman Kodak Co., Rochester, N. Y.  
 Mellette, F. M., Bethlehem Steel Co., New Castle, Del.  
 Miller, Robert A., Jr., 1125 Spruce St., Philadelphia, Pa.  
 Mullhaupt, Alfred, Jr., 25 School St., Bradford, Pa.  
 Nalbandian, Zaven A., 64 Pleasant St., Woburn, Mass.  
 Nilson, Maurice, Shawinigan Falls, Que., Canada.  
 Ott, Ludwig F., 34 Ridgewood Ave., Glen Ridge, N. J.  
 Parsons, J. U., 1109 Eighty-fourth St., Brooklyn, N. Y.  
 Power, Henry R., Worcester Polytechnic Institute, Worcester, Mass.  
 Pratt, William Beach, 514 Atlantic Ave., Boston, Mass.  
 Puhl, Louis J., Creighton Univ., Omaha, Nebr.  
 Rial, James H., Box 505, 122 Whitfield St., E. E., Pittsburgh, Pa.  
 Ritter, Horace L., 602 1/2 Washington St., Olean, N. Y.  
 Roast, Harold James, The James Robertson Co., Ltd., 142 William St.,  
 Montreal, Canada.  
 Rudman, C. F., Ironton, Ohio.  
 Satterfield, Russell L., 95 Beverly Ave., Morgantown, W. Va.  
 Saunders, A. T., The Pines, Chicopee, Mass.  
 Schroeder, James P., U. S. Dept. Agr., Bureau of Soils, Washington,  
 D. C.  
 Schultz, Arthur A., 336 N. Fifth St., Reading, Pa.  
 Scott, Henry Walter, 203 West 85th St., New York City.  
 Scribner, Bourdon W., 224 Fairview St., Piedmont, W. Va.  
 Simpson, Nathan A., 5529 Poplar St., Philadelphia, Pa.  
 Small, J. O., Hercules Club, Kenvil, N. J.  
 Sponable, Earl I., 9 Orchard St., Auburn, N. Y.  
 Straus, P., Calco Chemical Co., Lehigh Ave. & Edgemont St., Phila-  
 delphia, Pa.  
 Supple, Omer E., 2307 E. 69th St., Chicago, Ill.  
 Terry, H. Warren, Jr., 10 Hamilton Ave., Ossining, N. Y.  
 Thevenot, Gaston D., 200 Pleasant St., Milwaukee, Wisc.  
 Turner, Joseph L., 281 Greene Ave., Brooklyn, N. Y.  
 Tuttle, Neal, 469 Broadway, Cambridge, Mass.

Waldman, Louis I., 78 Willet St., Albany, N. Y.  
 Ward, Henry P., 308 William St., Middletown, Conn.  
 Weaver, Ralph M., 1332 Green Lane, Fern Rock, Philadelphia, Pa.  
 White, John J., 149 Broadway, New York City.  
 Wiehl, Arthur I., 240 E. 19th St., New York City.  
 Williams, Roger C., 45 Jaques Ave., Rahway, N. J.  
 Wilson, Ellery L., Rumford Chemical Works, Providence, R. I.  
 Wood, Percival I., Oriental Silk Printing Co., Haledon, N. J.  
 Wotring, Harry, Indiana Rubber & Insulated Wire Co., Jonesboro, Ind.  
 Woythaler, Max I., Box 481, Herkimer, N. Y.

## MEETINGS OF THE SECTIONS.

[Full accounts of all meetings should be sent to Secretary Charles L. Parsons Box 505, Washington, D. C.]

### CALIFORNIA SECTION.

The 92nd regular meeting was held September 19th. Program: "Colloids and Biology," by Dr. Martin H. Fischer, Professor of Physiology, University of Cincinnati. "The Use of Petroleum in Smelting Iron Ore," by Mr. A. E. Bourcoud.

BRYANT S. DRAKE, *Secretary*

### CHICAGO SECTION.

The regular monthly meeting was held October 13th. The paper of the evening was on "The Evolution of the Elements and Structure of Atoms," by Dr. W. D. Harkins, of the University of Chicago.

D. K. FRENCH, *Secretary*.

### CINCINNATI SECTION.

The 207th regular meeting was held October 11th. Program: "Exfoliation and Carbon Concentration in the Case-Hardening of Steel," by Edwin P. Stenger.

E. K. FILMS, *Secretary*.

### CLEVELAND SECTION.

The opening meeting of the year 1916-17 was held October 9th. Dr. Harry N. Holmes, head of the Chemistry Department of Oberlin College, spoke on "Some Recent Researches in Colloid Chemistry."

A. F. O. GERMANN, *Secretary*.

### CONNECTICUT VALLEY SECTION.

The 42nd regular meeting was held October 7th. Program: "Cooperation between the College and Industry," by Dr. M. L. Crossley.

R. J. MARSH, *Secretary*.

### DETROIT SECTION.

The 82nd regular meeting was held September 21st. Program: "Agricultural Chemistry: Its Present Status in the United States, and its Relation to the National Food Problem," by Dr. H. J.

Wheeler, of Boston, Mass., Manager of the American Agricultural Chemical Co.

JAMES H. BOGART, *Secretary*.

#### EASTERN NEW YORK SECTION.

The 68th meeting was held at Saratoga Springs, September 23rd. Dr. J. H. Stoller, Professor of Geology at Union College, spoke on "Geology and Geochemistry of the Saratoga Quadrangle."

ALBERT J. SALATHE, *Secretary*.

#### INDIANA SECTION.

The first fall meeting was held October 13th. Dr. R. H. Ransom addressed the section on "Chemical Science in Indiana." Officers were elected for the ensuing year as follows: F. C. Atkinson, *President*; C. M. Hargrave, *Vice-President*; H. W. Rhodehamel, *Secretary-Treasurer*.

H. W. RHODEHAMEL, *Secretary*.

#### LEXINGTON SECTION.

The Section held its 34th regular meeting October 12th. Program: "The Chemistry of Bread-Baking," by Mr. R. C. Dabney.

P. L. BLUMENTHAL, *Secretary*.

#### MARYLAND SECTION.

The 15th meeting was held October 21st. Dr. W. W. Randall, of the Maryland State Board of Health, presented a paper on "The Hydrolysis of Ethyl Sulfuric Acid."

FRANK M. BOYLES, *Secretary*.

#### NEW YORK SECTION.

The 1st regular meeting of the session 1916-17 was held October 13th, in conjunction with the New York Sections of the American Electrochemical Society, and the Society of Chemical Industry. Program: "Why Our Chemical Import Statistics Should be Overhauled," by Bernhard C. Hesse.

CHAS. F. ROTH, *Secretary*.

#### PHILADELPHIA SECTION.

The regular meeting was held October 19th. Program: "Early History of Chemical Industry in Philadelphia," by Dr. Samuel P. Sadtler.

J. HOWARD GRAHAM, *Secretary*.

#### PITTSBURGH SECTION.

The 129th regular meeting was held September 21st. Program: W. C. Cope, (a) "Revision of Our Chemical Import Statistics," (b) "Ten-Year Index to Chemical Abstracts;" A. V. Bleininger, "The Properties of Some European Bonding Clays."

The 130th meeting was held October 19th. Program: "The Viscosity of Blast Furnace Slags," by A. L. Field; "The Extraction of Cerium and Preparation of Some of its Salts," by C. T. Vogt.

W. C. COPE, *Secretary*.

# PUGET SOUND SECTION.

The Section met September 25th. Illustrated Lecture: "The Genesis of the Elements," by Prof. W. D. Harkins. Chairman of the Chicago Section.

H. L. TRUMBULL, *Secretary*.

# RHODE ISLAND SECTION.

The October meeting was held October 11th. Mr. C. F. Quaintance, of the Herold China and Pottery Co., of Golden, Colorado, spoke on "Made in America Porcelain," and Mr. W. W. Case, of Denver, Colorado, spoke on "Denver Fire Clay Products."

ROBERT F. CHAMBERS, *Secretary*.

# ROCHESTER SECTION.

A meeting was held October 2nd. Program: "Photo-Engraving," by A. J. Newman.

The regular meeting was held October 16th. Mr. H. A. Carpenter, of West High School, spoke on "The Teaching of Elementary Chemistry."

H. H. TOZIER, *Secretary*.

# ST. LOUIS SECTION.

A meeting was held October 2nd. Program: "The New United States Pharmacopoeia," by Dr. C. E. Caspari.

GEO. LANG, JR., *Secretary*.

# SYRACUSE SECTION.

The following have been elected as officers of the section for the ensuing year: G. M. Berry, *President*; E. J. Wall, *Vice-President*; R. S. Boehner, *Secretary*; R. S. Fleming, *Treasurer*; E. S. Johnson, *Councilor*.

R. S. BOEHNER, *Secretary*.

# UNIVERSITY OF ILLINOIS SECTION.

A joint meeting was held with the Chemical Club of the University of Illinois, October 3rd. Miss Marian E. Sparks spoke on "Chemical Literature and its Use."

G. D. BEAL, *Secretary*.

# WISCONSIN SECTION.

The October meeting was held October 10th. Prof. Bradley Stoughton, Secretary of the American Institute of Mining Engineers, spoke on "The Constitution of Steel."

L. F. AUGSPURGER, *Secretary*.



# Proceedings.

## COUNCIL.

President Herty appointed the following as members of the Committee on Dyestuffs for the U. S. Bureau of Printing and Engraving: J. Merritt Matthews, *Chairman*, Allen Rogers, E. F. Roeber.

MEMBERS ELECTED BETWEEN OCTOBER 15 AND NOVEMBER 15, 1916.

- Acheson, John L., 743 Hill Ave., Wilkinsburg, Pa.  
Allen, E. J., Defiance, Ohio.  
Anderson, Arthur K., 307 Manitou St., Northfield, Minn.  
Bache-Wiig, John, 507 Cumberland Ave., Portland, Maine.  
Benjamin, Edward O., 177 Hillside Ave., Newark, N. J.  
Berg, Eysten, Room 659, 200 Fifth Ave., New York City.  
Berk, Paul Felix, 1 Fenchurch Ave., London, E. C., England.  
Bicknell, Richard S., 65 Prospect St., East Orange, N. J.  
Blodgett, W. A., 34 Hickok Place, Burlington, Vt.  
Blue, Thos. G., Prescott, Ariz.  
Bock, John E., 3322 Walnut St., Milwaukee, Wis.  
Booraem, J. Francis, 52 Vanderbilt Ave., New York City.  
Bronfenbrenner, Jacob, Western Pennsylvania Hospital, Pittsburgh, Pa.  
Brown, Ralph, 212 McCoy St., Joplin, Mo.  
Bunce, Allen H., 824 Healy Bldg., Atlanta, Ga.  
Burdette, J. C., 1014 So. Kildare Ave., Chicago, Ill.  
Capen, George P., 479 Sherman St., Canton, Mass.  
Clarke, Walter Wm., 1521 Jefferson St., Latrobe, Pa.  
Clements, Hubbard, Achæan Club, 2521 Channing Way, Berkeley, Calif.  
Coutlis, S. G., 224 Sixth Ave., N. E., Calgary, Alberta, Canada.  
Curran, Carleton E., 91 Sixteenth Ave., Columbus, Ohio.  
Davidson, Philip L., 515 Stewart Ave., Ithaca, N. Y.  
Davies, Meurig Lloyd, Standard Chemical Iron & Lumber Co., 1104 Royal Bank Bldg., Toronto, Canada.  
Davis, Luther, 53 Hillsdale St., Dorchester, Mass.  
Davis, R. E., 6118 Kenwood Ave., Chicago, Ill.  
de Giovellina, E. Colonna, The Gifford, 1348 Robson St., Vancouver, B. C., Canada.  
Diggs, Sterling H., 436 Cleveland Ave., Whiting, Ind.  
Drayton, Henry C., 829 Park Ave., New York City.  
Du Puy, Sam. W., Pierce, Fla.  
Emberg, George, 712 Aldine Ave., Chicago, Ill.  
Evans, John, 67 Surrey St., Sheffield, England.  
Everett, Fred T., 264 Washington St., Binghamton, N. Y.  
Fahlman, Everett G., 516 So. Division St., Ann Arbor, Mich.  
Ferguson, Robert, Y. M. C. A., Baltimore, Md.  
Fischelis, Robert P., 828 N. Fifth St., Philadelphia, Pa.  
Fletcher, John, 103 No. Portland Ave., Brooklyn, N. Y.  
Foster, L. F., 45 Harkness Ave., Pasadena, Calif.  
Fox, Paul N., 250 Columbia Ave., Pomona, Calif.

Fukushima, Ikuzo, c/o Chemical Laboratory, Johns Hopkins University, Baltimore, Md.

Funke, Carl A., 160 West 142nd St., New York City.

Geiger, Albert C., Jr., P. O. Box 197, Rhinebeck, N. Y.

Glennner, Isadore, 1418 W. 13th St., Chicago, Ill.

Goodwillie, Edward, c/o The Solvay Process Co., Detroit, Mich.

Gordon, Edith M., College of Industrial Arts, Denton, Texas.

Grimes, E. G., Box 1137, Fresno, Calif.

Hale, R. W., Jr., Central Y. M. C. A., Baltimore, Md.

Hall, Frank, Mass. Inst. of Tech., Boston, Mass.

Hancock, Henry E., 1961 Winona St., Chicago, Ill.

Haring, Malcolm M., Graduate College, Princeton, N. J.

Harris, Joel S., 619 No. 55th St., Philadelphia, Pa.

Hasselgren, Ragnar E., 127 W. Hortter St., Germantown, Philadelphia, Pa.

Hawkins, Wales M., 32 So. Converse Hall, Burlington, Vt.

Hougen, Olav A., 619 West Johnson St., Madison, Wis.

Hutson, Harry M., Armour & Co., Matanzas, Cuba.

Huyett, Amos W., 727 N. Fourth St., Reading, Pa.

Joy, John B., 61 Broadway, New York City.

Joyce, William Thos., 22 Maynard St., Pawtucket, R. I.

Khachadorian, Aram H., 41 Walker St., Cambridge, Mass.

Kitchin, Donald W., 203 Bay State Road, Boston, Mass.

Kramer, Richard Lee, Livingston Hall, Columbia University, New York City.

Latshaw, Max, 1714 Jefferson St., Duluth, Minn.

Lederer, E. R., 1409 Carter Bldg., Houston, Texas.

Lewis, A. L., c/o Braden Copper Co., Sewell, Rancagua, Chile.

Lewis, Howard W., 202 E. 8th St., Chester, Pa.

Lisse, Martin W., Hinman House, Evanston, Ill.

Loeb, Edward H., 143 E. Frambes Ave., Columbus, Ohio.

Luce, John W., c/o University of Nevada, Box 183, Reno, Nev.

Lynn, Arthur H., 40 Westminster Palace Gardens, Victoria St., London, S. W., England.

Lyon, Dorsey A., U. S. Bureau of Mines, Salt Lake City, Utah.

Marcus, Siegbert Theodore, 915 Elsmere Place, Bronx, New York City.

Matheson, H. W., Canadian Electro Products Co., Shawinigan Falls, Que., Canada.

Matte, Andrew L., 371 Atwater St., Detroit, Mich.

McKellog, C. S., Med. Bldg., University of Buffalo, Buffalo, N. Y.

Miller, Benj. L., 543 Sixty-ninth Ave., West Allis, Wis.

Moore, Joseph, Jr., Widener Bldg., Philadelphia, Pa.

Moscowitz, Abraham, 136 East 48th St., New York City.

Moulton, Seth A., 120 Exchange St., Portland, Maine.

Mudge, William A., Albright College, Myerstown, Pa.

Mueller, F. A., 212 So. 25th St., Omaha, Nebr.

Munster, Julius K., c/o T. C. T. & R. R. Co., By-product Department, Fairfield, Ala.

Nakai, S., c/o Miike Coal Mine, Ohinuta, Fukuokaken, Japan.

Neal, Charles B., J. H. Williams & Co., Brooklyn, N. Y.

Nicholls, Jesse C., Picatinny Arsenal, Dover, N. J.

O'Brien, Ruth, Iowa State College, Chemistry Department, Ames, Iowa.

Page, Irvine H., Woodstock Drive, Indianapolis, Ind.

- Peter, Rudolph W., 781 McKendrie St., San Jose, Calif.
- Price, Weston A., 8803 Euclid Ave., Cleveland, Ohio.
- Richert, Theodore, P. O. Box 27, Portsmouth, Va.
- Roberts, Arthur, 608 So. Dearborn St., Chicago, Ill.
- Roberts, W. A., Dept. of Chem., Iowa State College, Ames, Iowa.
- Roon, Leo, 215 Fulton St., New York City.
- Russell, G. A., 13 E. Wash. Ave., Orlando, Fla.
- Schaefer, Hugo H., 115 West 68th St., New York City.
- Schepmaes, C. H., Dept. of Chem., Northwestern University, Evanston,

## III.

- Scheuermann, George, Jr., 2514 Chippewa St., New Orleans, La.
- Schrack, Lloyd E., 240 Third St., Niagara Falls, N. Y.
- Sharp, C. M., Shortridge High School, Indianapolis, Ind.
- Shimeall, Karl W., Elks Home, Florence, Colo.
- Skoglund, Herbert, 6353 Yale Ave., Chicago, Ill.
- Slater, Lewis Cecil, 510 St. Hypolite St., Baton Rouge, La.
- Sloan, Alexander, Cumberland, Md.
- Smith, George Otis, 35 South Converse Hall, Burlington, Vt.
- Stine, C. M., Drawer 424, Chester, Pa.
- Straus, Sydney, 690 Putnam Ave., Brooklyn, N. Y.
- Strode, F. Brinton, 208 S. McAllister St., State College, Pa.
- Sutphen, Martin E., 838 Ackerman Ave., Syracuse, N. Y.
- Swasey, E. K., Beloeil, P. Q., Canada.
- Tanner, W. Lee, Box 249, Wilmington, Del.
- Thompson, C. D., East Windsor Hill, Conn.
- Thompson, Henry B., 320 Broadway, New York City.
- Tilden, Philip S., 3500 Grays Ferry Road, Philadelphia, Pa.
- Trolander, Elmer Wilcox, 4051 Ellis Ave., Chicago, Ill.
- Turull, Thos. F., Muralla 2, Havana, Cuba.
- Ulmer, Carl D., 162 E. Water St., Middletown, Pa.
- Wagner, Edward L., 124 Willett St., Jamaica, L. I., N. Y.
- Wagner, Frederick H., Rogers Ave. & Pimlico Road, Station E., Baltimore, Md.
- Ware, Gertrude M., 417 West 120th St., New York City.
- Weesner, Carl W., 1004 Fairview St., Youngstown, Ohio.
- Wescott, Ernest W., 106 Trowbridge St., Cambridge, Mass.
- Wheeler, Frank C., 401 N. West St., Syracuse, N. Y.
- Williamson, M. A., 35 E. 41st St., New York City.
- Wiltrout, C. B., Guanica Centrale, Ensenada, Porto Rico.
- Witherell, Archie Lee, 96 Doty St., Fond du Lac, Wis.
- Workman, Albert C., Bethany, W. Va.
- Zucker, Richard D., Franklin Baker Co., Imlay & Commerce Sts., Brooklyn, N. Y.

## CORPORATION MEMBER.

Pennsylvania Rubber Co., Jeannette, Pa.

## MEETINGS OF THE SECTIONS.

[Full accounts of all meetings should be sent to Secretary Charles L. Parsons, Box 505, Washington, D. C.]

## ALABAMA SECTION.

The regular meeting was held October 7th. Program: "Some In-

“Interesting Data on the Decomposition of Ammonia by Heat,” by Mr. Julius K. Munster.

W. H. BRUNS, JR., *Secretary*.

#### AMES SECTION.

At the meeting held October 19th, the following officers were elected for 1917: *President*, C. C. Fowler; *Vice-President*, C. A. Mann; *Secretary-Treasurer*, A. R. Lamb; *Councilor*, W. F. Coover.

W. C. GAEHLER, *Sec.*

#### CALIFORNIA SECTION.

The 93rd meeting of the Section was held October 21st. Program: “The Outlook for Cheap Oxygen,” by Dr. F. G. Cottrell; “Modern Views of Metallic Conduction,” by Dr. G. E. Gibson.

BRYANT S. DRAKE, *Secretary*

#### CHICAGO SECTION.

The monthly meeting was held November 17th. Program: “Notes on the Secretion and the Chemistry of the Human Gastric Juices,” by Dr. A. J. Carlson.

D. K. FRENCH, *Secretary*

#### CINCINNATI SECTION.

The 208th regular meeting was held November 15th. Program: “Methods of Isolation and Identification of *B. Coli* Now Used at the Cincinnati Filtration Plant,” by S. J. Hauser; “Relation of Microorganisms to the Loss in Head in Rapid Sand Filters,” by J. W. Ellms and S. J. Hauser.

ELLERY K. FILES, *Secretary*

#### CLEVELAND SECTION.

The regular meeting was held November 13th. Program: “Steel and Some Recent Improvements in Its Manufacture,” by L. Selmi, Otis Steel Co.

A. F. O. GERMANN, *Secretary*.

#### COLUMBUS SECTION.

The monthly meeting was held November 10th. Program: “The Electrolytic Production of Antimony,” by Prof. D. J. Demorest. The following officers were elected for the ensuing year: *President*, Dr. George F. Weida; *Vice-President*, Wm. J. McCaughey; *Secretary-Treasurer*, Robert C. Hummel; *Councilor*, Dr. J. R. Withrow.

R. C. HUMMEL, *Secretary*.

#### CONNECTICUT VALLEY SECTION.

The 43rd regular meeting of the Section was held November 4th. Program: “Some Effects of Impurities in Boiler Feed Water,” Dr. C. S. Williams; “The Production of Aromatics from Petroleum,” Dr. E. C. Stone.

R. J. MARR, *Secretary*.

#### DETROIT SECTION.

The 84th regular meeting was held in conjunction with the Detroit Engineering Society, November 17th. Program: “Synthetic Resins,” by Dr. Leo. H. Baekeland.

J. H. BOONET, *Secretary*.





